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DIAGONAL SUMMATION OF NUMBERS IN ARITHMETICAL PROGRESSION

By

PROF. M. L. CHANDRATREYA, M.A.

AND

D. R. KAPREKAR, B.Sc., S.T.C.

THIS article brings to the notice some interesting properties of the various constants lgr and Rgr described in the article of the *Bombay University Journal*, November 1939, pp. 17-21.

By *diagonal process* we mean writing down a series of numbers one below the other, the lower number always written down the upper number omitting the first digit on the right-hand side: thus resembling the construction of a diagonal of a rectangle, e.g.—

157	is applying the process to the
157	numbers 157, 157, 157.
157	

If we take a single number and write it down diagonally again and again and take the sum as we do in the usual process of multiplication, the sum is a Demlo number. Thus for 175,

175	=19 (4) ₃ 25.
175	
175	
175	
175	
175	

1944425	

This process is described already in the *Bombay University Journal*, 1938, pp. 12-13, as demlofication of N. This process for shortness will be called as 'dialing', and we shall 'dial the number' when required.

We now consider a series of numbers in A. P. such as N, $N+d$, $N+2d$, $N+3d$with d as the common difference. Dialing gives some peculiar properties. We shall bring them out by some particular examples. Take $N=134$, $d=6$. Thus

dialing ten numbers 134, 140, 146, 152.....we get the sum8148 148 134.

It will be noted that the group 148 will be repeating again and again.

Take $N=452$, $d=9$; dialing for seven numbers 452, 461, 470.....gives the sum 1111062. Here the digit one will go on repeating again and again as the process is continued. Such repeating numbers will be henceforward named as 'recurring' groups.

We do not take into account here the figures at the extreme right in this diagonal summation—*e.g.*, 134 in the first example and 062 in the second example above. These will be called as 'neglected' parts at the extreme right. The number of digits in the neglected part will be nearly the same as the number of digits in the original number N . We assume for the present that for any values of N and d the dial process gives recurring groups.

The recurring groups can be conveniently divided into 4 classes depending upon the number d of the common difference of the A. P.

Class I:—When d of A. P. is a multiple of nine but not of ten at the same time—*e.g.*, 9, 27, 45,.....but not 90, 450.....In this case the recurring group will consist of a single digit. These can be 0, 1, 2,.....8, 9 repeated again and again—*e.g.*, $N=165$, $d=18$. Here the recurring group figure will be 1 and 095 the neglected part. For $N=234$, $d=9$, the recurring figure is 8 and 64 is the neglected part.

Class II:—When d of the A. P. is a multiple of three but is not at the same time a multiple of nine or ten—*e.g.*, 6, 12, 105 but not 27, 60, etc. Here the recurring group will contain three digits in every case. These recurring groups will be described B_r groups. Their values will be found to be—

$$B_1 = 037 = B_1 \times 1$$

$$B_2 = 074 = B_1 \times 2$$

$$B_4 = 148 = B_1 \times 4$$

$$B_5 = 185 = B_1 \times 5$$

$$B_7 = 259 = B_1 \times 7$$

$$B_8 = 296 = B_1 \times 8$$

Any of these recurring groups or their cyclic changes will be seen to be repeated. By cyclic change we mean that the digits are to be written out in a circle in order and to be read beginning with any digit. Thus 037 may be read as 037, 370, 703.

As an example of this class take $N=123$, $d=12$. The numbers dialed give

$$\begin{array}{r}
 123 \\
 135 \\
 147 \\
 159 \\
 171 \\
 \hline
 851 \ 851 \ 851 \ 73
 \end{array}$$

Here the repeating group is 851. This is B_6 with a cyclic change. Let $N=312$, $d=21$ then dialing gives.....740 740 740 42. Here the recurring group is B_2 with a cyclic change.

*Class III:—*When d of the A. P. is neither a multiple of three nor that of ten—*e.g.*, 5, 7, 22.....In this case the recurring group consists of nine digits. These will be called C_r groups. They are the following:—

$$\begin{aligned}
 C_1 &= 098765432 = C_1 \times 1 \\
 C_2 &= 197530864 = C_1 \times 2 \\
 C_4 &= 395061728 = C_1 \times 4 \\
 C_5 &= 493827160 = C_1 \times 5 \\
 C_7 &= 691358024 = C_1 \times 7 \\
 C_8 &= 790123456 = C_1 \times 8
 \end{aligned}$$

Here again the recurring group may consist of the cyclic change. Thus $C_2=197530864$ will appear as 753086419 or 864197530 or 308641975, etc. We shall consider only two examples. Take $N=112$, $d=4$, and 23 number of terms in A. P., then the sum is,

$$\text{.....} \underline{172} \ \underline{839506172} \ \underline{839506172} \ 72$$

Here the recurring group is 839506172. This is the same as C_4 with a cyclic change. Take $N=1213$, $d=32$, and 22 number of terms in A. P., then the sum is,

$$\underline{60} \ \underline{493827160} \ \underline{493827160} \ 363$$

The recurring group is C_5 .

*Class IV:—*When the common difference is a multiple of ten. In this case express $d=a \times 10^n$ and find under which cases a falls. If a is a multiple of nine the recurring group will be the one described in case I. It will consist of only one digit. If a is a multiple of three the recurring group consists of three digits given by the B_r series. If a is not a multiple of 3 or 9 the repeating group will come out as described in case III, *viz.*, any of

the numbers in C_r series—e.g., $d=340=34 \times 10^1$ and 34 is not a multiple of 3 or 9. The recurring group here will be found to be 691358024 or its cyclic change. If $d=1200=12 \times 10^2$ and 12 is a multiple of three. This is case II. If $d=270=27 \times 10^1$ and 27 is a multiple of 9, the recurring group comes under case I.

A reference to the *Bombay University Journal*, November 1939, pp. 17-21 will show that the constants B_r are the constants lgr on page 17 occurring when rr' is a multiple of three. Similarly the constants C_r are some of the values of lgr when rr' is not a multiple of 3, 9 or 10, as given on page 21. As for the constants in case I they come under VII at page 15 in that *Journal*.

It appears that the constants recurring in the diagonal process of A. P. numbers are closely related to the constants occurring in the products of linear demlo numbers. A theoretical discussion in this connection will have its place in due time.

[We thank the University of Bombay for the research grant given to one of us—(D. R. K.)].

(College of Engineering, Poona)
Khare's Wada, Camp Deolali.

[Received July 10, 1940]

GENERAL EXPRESSION FOR THE PRODUCT OF DEMLO NUMBERS

By

D. R. KAPREKAR, B.Sc., S.T.C.

(Communicated by Prof. M. L. Chandratreya)

PRODUCT of linear Demlo numbers has been discussed in detail in the *Bombay University Journal*, November 1939. In this article we would discuss the product of two Demlo numbers of any type.

2. A linear Demlo number consists of only one digit r repeated n times and is written as

$$\begin{aligned}(r)_n &= r(1)_n \\ &= r(10^{n-1} + 10^{n-2} + \dots + 10 + 1) \\ &= r \left(\frac{10^n - 1}{9} \right) \dots \dots \dots (A)\end{aligned}$$

In particular

$$(9)_n = 9 \left(\frac{10^n - 1}{9} \right) = 10^n - 1 \dots \dots \dots (A')$$

3. A binary Demlo number has three parts. The first part is M, the middle part is $(r)_n$ and the last part is P such that $M + P = (r)_{n'}$. The number of digits in M and P is the same, viz., n' . The number is represented by $M(r)_nP$ where $M + P = (r)_{n'}$.

$$\begin{aligned}\text{Here } M(r)_nP &= P + (r)_n 10^{n'} + M \times 10^{n+n'} \\ &= (r)_n - M + (r)_n 10^{n'} + M \times 10^{n+n'}\end{aligned}$$

and using the formula (A) before, we get—

$$\begin{aligned}M(r)_nP &= r \left(\frac{10^{n'} - 1}{9} \right) - M + r \left(\frac{10^n - 1}{9} \right) 10^{n'} + M \times 10^{n+n'} \\ &= \frac{r}{9} (10^{n+n'} - 1) + M (10^{n+n'} - 1) \\ &= \left(M + \frac{r}{9} \right) (10^{n+n'} - 1) \\ &= (9M + r) \left(\frac{10^{n+n'} - 1}{9} \right) \dots \dots \dots (B)\end{aligned}$$

Also noting that $\frac{10^{n+n'}-1}{9} = (1)_{n+n'}$

we get $M(r)_nP = (9M+r) \times (1)_{n+n'}$ (C)

4. The formulas (A), (B), (C) given before will be stated again for ready reference :

$$(r)_n = r \times \left(\frac{10^n - 1}{9} \right) \dots \dots \dots (A)$$

$$M(r)_nP = (9M+r) \times \left(\frac{10^{n+n'} - 1}{9} \right) \dots \dots \dots (B)$$

$$M(r)_nP = (9M+r) \times (1)_{n+n'} \dots \dots \dots (C)$$

5. In such a number, $M(r)_nP$, $(n+n')$ will be called as the length of that number, *e.g.*, the length of 2478888 621 is 7 and that of 54723 is 3.

In two binary Demlo numbers if n and n' are the same respectively then they will be referred to as similar Demlo numbers. If the values of n and n' are not the same, they will be called as non-similar.

Thus 3177746, 2566641 are similar each of length 5 ; while 2499975, 377774 are non-similar though of the same length.

6. Take two similar Demlo numbers :

$$M(r)_nP \text{ and } M'(r')_nP'$$

Then by (B)—

$$M(r)_nP \times M'(r')_nP' = \frac{(9M+r) \times (9M'+r') \times (10^{n+n'} - 1)^2}{81}$$

$$= \frac{G}{81} \times (10^{n+n'} - 1)^2$$

where G stands for the product $(9M+r)(9M'+r')$. The value of the product will depend upon the consideration of the value of

the expression $\frac{G}{81} \times (10^{n+n'} - 1)^2 = \frac{G}{81} (9)_{n+n'}^2 \dots \dots \dots$ by (A)

Now

$$(9)_{n+n'}^2 = 81 \times (1)_{n+n'}^2$$

$$= (9)_{n+n'-1} \quad 8 \quad (0)_{n+n'-1} 1$$

(See the article Wonderful Demlo Numbers in Mathematics, *Student*, Vol. VI, p. 69, and the *Bombay University Journal*, November 1939, p. 16).

7. First we consider the value of $\frac{G}{81}$ in relation to the factors of G and 81.

$$\frac{G}{81} = 3 \times 3 \times 3 \times 3 \times 3 \times 3 \times 27 \times 9 \times 9$$

G is a composite number and the factors can be 3, 9, 27 or 81 or it may have any other factor except these. Various cases arise.

Case I.—When G is a multiple of 3 but not of ten or nine, $G/81$ reduces to $\frac{g'}{27} = g' \times \cdot\dot{0}3\dot{7}$ where $\frac{1}{27}$ = the recurring decimal $\cdot\dot{0}3\dot{7}$. The recurring period contains three digits; hence the product $g' \times \cdot\dot{0}3\dot{7}$ will contain a recurring period of three digits, i.e., $\frac{G}{81}$ is a recurring decimal in which the recurring group consists of three digits.

Case II.—When G is a multiple of 9 but not of ten, similar arguments will give $\frac{G}{81} = \frac{g''}{9} = g'' \times \cdot 1'$ and $\frac{G}{81}$ is a recurring decimal in which the recurring group consists of one digit only.

Case III.—When G is a multiple of 27, $\frac{G}{81} = \frac{g'''}{3} = g''' \times \cdot 3'$ and the recurring group consists of one digit only.

Case IV.—When G is not a multiple of 3, 9 or 27, their $\frac{G}{81} = G \times \cdot\dot{0}1234567\dot{9}$ and has 9 figures in the recurring part.

If G has a factor 10 or its power, then these zeroes will only shift the position of the decimal point and the case will reduce to one of the four cases considered already.

8. The other factor $(10^{n+n'}-1)^2$ has been already evaluated in VI and the conclusion is that the actual value of the product of the two similar Demlo numbers will contain recurring groups of 1, 3 or 9 digits according to the case under which it falls. It is also obvious that because $(10^{n+n'}-1)^2 = (9)_{n+n'-1}8(0)_{n+n'-1}1$ where repeated digits 9 and 0 occur, the product will contain two recurring groups. Thus the product will contain two recurring groups of one, three or nine digits, depending upon the value and peculiarities of G. An important feature in the formula of the product is that even though $\frac{G}{81}$ is a recurring decimal yet its product with the value of $(10^{n+n'}-1)^2$ must give an integral number.

9. A few corollaries may be obtained from the results discussed.

If r and r' are each multiples of three, then—

$$\frac{G}{81} = \frac{(9M+r)(9M'+r')}{81} = \frac{(9M+3m)(9M'+3m')}{81} = \frac{(3M+m)(3M'+m')}{9}$$

where $r=3m$ and $r'=3m'$ and $\frac{G}{81}$ will contain recurring group of one digit only and the result thus stated.

Corollary I:—The product of two Demlo numbers in which the repeating middle digits are 3, 6 or 9, will contain repeating groups consisting of one digit only.

Corollary II:—Squares of Demlo numbers in which the repeating middle digits are 3, 6 or 9, will contain repeating groups consisting of one digit only.

If only r or r' is a multiple of three, then $\frac{G}{81}$ reduces to $\frac{g'}{27}$ and the product will come under case I, and hence—

Corollary III:—The product of two Demlo numbers in which the repeating digit of one is a multiple of three and that of the other is not a multiple of three, will contain repeating groups consisting of three digits. Similar arguments give—

Corollary IV:—The product of two Demlo numbers in which the repeating digits are not multiples of three, i.e., are 1, 2, 4, 5, 7 or 8, will contain repeating groups of nine digits.

10. Product of two non-similar Demlo numbers can be discussed on the same lines and will form part of the next article. But a slight indication may be given.

For two non-similar numbers the product is expressed as

$$\frac{(9M+r)(9M'+r')}{81} \cdot \left(10^{\frac{n_1+n'_1}{-1}}\right) \left(10^{\frac{n_2+n'_2}{-1}}\right)$$

Here the peculiarities will depend upon the factors of 81. The product of three similar Demlo numbers $M(r)_nP$, $M'(r')_nP'$ and $M''(r'')_nP''$ will be equal to

$$\begin{aligned} & \frac{(9M+r)(9M'+r')(9M''+r'')}{729} \times \left(10^{\frac{n+n'+n''}{-1}}\right)^3 \\ &= \frac{H}{729} \left(10^{\frac{n+n'+n''}{-1}}\right)^3 \end{aligned}$$

and will depend upon the recurring property of $\frac{1}{729}$ contains a recurring period of 81 figures and so the highest recurring group expected in the product of three Demlo numbers will be of 81 figures. The method thus may be extended.

11. A few examples are given here.

Ex. 1. Take $15(6)_5 51 \times 14(3)_5 19$.

Here $n=5$, $n'=2$. $G=(9 \times 15+6) \times (9 \times 14+3)=141 \times 129=9 \times 43 \times 47$. Here 9 is a factor and the product must contain recurring groups of one figure. Actual product gives—

$$15(6)_5 51 \times 14(3)_5 19 = 224(5)_4 106(4)_4 669.$$

The following results can also be put down side by side with the result already obtained.

$$15(6)_5 51 \times 14(3)_5 19 = 224(5)_4 106(4)_4 669.$$

$$15(6)_4 51 \times 14(3)_4 19 = 224(5)_3 106(4)_3 669.$$

$$15(6)_3 51 \times 14(3)_3 19 = 224(5)_2 106(4)_2 669.$$

$$15(6)_2 51 \times 14(3)_2 19 = 224(5)_1 106(4)_1 669.$$

$$15(6)_1 51 \times 14(3)_1 19 = 224 \ 106 \ 669.$$

Thus when $n=1$ the recurring figures do not occur, and moreover the number of repetitions is one less in the product than the number of repetitions in the original Demlo numbers. Thus the general equation representing this equation may be written as—

$$\{15(6)_n 51\} \times \{14(3)_n 19\} = 224(5)_{n-1} 106(4)_{n-1} 669.$$

The numbers 224, 106, 669 will be called as constants; 224 as the left constant and denoted by lc , 106 as the middle constant and denoted by mc , and 669 as the right constant and denoted by rc . The repeated digit 5 will be called dl , for it is the digit on the left side and the other digit 4 will be called dr , for it is the digit on the right side. Thus the most general form representing the product $M(r)_n P \times M'(r')_n P'$ will be—

$$lc(dl)_{n-k} mc(dr)_{n-k} rc.$$

$$\text{Ex. 2. } \{22(6)_n 44\}^2 = 513(7)_{n-2} 6750(2)_{n-2} 2736.$$

In particular if $n=2$,

$$\{226644\}^2 = 513 \ 6750 \ 2736.$$

$$\text{Ex. 3. } \{17(6)_8 49\} \times \{20(4)_8 24\}.$$

$$\text{Here } \frac{G}{81} = \frac{159 \times 184}{81} = \frac{53 \times 184}{27}. \text{ Thus the recurring groups}$$

contain three digits. The value of the product can be actually seen to be—

$$\begin{aligned} & 361(185)_3 1129(481)_3 5176 \\ & = 361 \ 185 \ 185 \ 1129 \ 481 \ 481 \ 5176 \dots\dots\dots(i) \end{aligned}$$

Similar consideration of

$$\{17(6)_9 49\} \times \{20(4)_9 24\} \text{ and}$$

$$\{17(6)_{10} 49\} \times \{20(4)_{10} 24\}$$

gives the two products as

$$361(185)_2 177961(481)_2 5176 \dots \dots \dots (ii) \text{ and}$$

$$361(185)_2 184\ 46\ 281\ (4\ 81)_2 5176 \dots \dots \dots (iii)$$

Comparison of (i), (ii), (iii), shows that the constants lc and rc in each are the same and the middle constants only change taking the values 1129, 177961 and 18446281 respectively, when $n=8, 9, 10$, respectively. If we take $n=11, 12, 13$ respectively, these middle constants will again reappear in the same order. But in the value of the products the repeating groups will have one more repetition. Thus—

$$\begin{aligned} & \{17(6)_{11} 49\} \times \{20(4)_{11} 24\} \\ &= 361(185)_3 1129(481)_3 5176. \end{aligned}$$

These middle constants will be called as rotating constants.

$$\text{Ex. 4. } \{24(5)_{24} 31\} \times \{26(7)_{24} 51\}$$

Here $\frac{G}{81} = \frac{221 \times 241}{81}$ and cannot be reduced and hence the repeating groups must contain 9 digits each. The actual value of the product can be found to be—

$$657(543209876)_2 54319672(567901234)_2 56790781.$$

By changing the value of n the values of lc and rc remain unchanged, but the value of mc changes and may take any one of nine values in order and rotation. Thus in such cases of products there are nine rotating constants. Calculation of the various quantities lc, mc, rc, dl, dr , can form a subject matter of much more future detailed description.

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PEDAL EQUATIONS OF A CIRCLE

By

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THE p-r or pedal equations of a number of simple curves are to be found in any text book dealing with geometrical applications of Calculus. We find, for instance, that the pedal equation of a straight line is $p=a$, that of a circle with the pole on the circumference is $2ap=r^2$, and so on. But there is no mention of the simplest case of all, *viz.*, the equation for a circle of radius a with the centre at the pole. This led me to investigate into the matter and I got some curious and interesting results which are embodied in the present article.

The scope of utility of pedal equation for any curve is quite limited, the more so for a circle ; the reason is that the geometry of the circle is so simple that it is almost invariably applied directly to problems. It may be remarked that the equations (1) and (2) represent some simple geometrical property of the circle.

As has already been noted, the geometry of the circle leads at once to the equation

$$p=r \tag{1}$$

as the pedal equation when the centre is at the pole. Now, (1) would represent any one of the system of concentric circles, and to obtain, therefore, the equation of a particular circle of radius a we must use

$$p=r=a \tag{2}$$

as the required equation (or equations). This includes $r=a$, which is the polar equation of the circle and sufficient to define it ; there is also, in (2), the equation $p=a$, which is the pedal equation of some straight line as well. In an attempt to obtain a definite circle we have thus obtained on one hand some more-than-sufficient conditions, and on the other hand an additional locus. Of course, if both the equations of (2) are taken together,

the second locus goes out of consideration, but still the question of redundancy remains.

Next, the pedal equation of an ellipse with the centre at the pole is

$$\frac{a^2 b^2}{p^2} = a^2 + b^2 - r^2. \quad (3)$$

When $b \rightarrow a$, the ellipse reduces to the circle of radius a . Therefore the above gives

$$\frac{a^2}{p^2} = 2a^2 - r^2 \quad (4)$$

as another pedal equation of the circle in question.

If the focus of the ellipse be the pole, the pedal equation is given by

$$\frac{b^2}{p^2} = \frac{2a}{r} - 1 \quad (5)$$

and, by making the eccentricity tend to zero, we get yet another form of the pedal equation of the circle, *viz.*,

$$\frac{a^2}{p^2} = \frac{2a}{r} - 1. \quad (6)$$

In fact, we shall presently see that almost all pedal equations represent a circle amongst other loci.

2. In general we have to specify three characteristics of a curve in order to define it uniquely; these are its shape (or nature), its size and its position. The Cartesian or polar equation helps us to arrive at all these things simultaneously. So, in this case a single equation suffices to define a curve. The p - r equation can not give all the three characteristics, and therefore the pedal equation does not represent a single curve. Both coordinates, p and r , depend only on the position of the pole in relation to the curve and are independent of the direction of the initial line. Hence it is obvious that if a curve be rotated about the pole, the pedal equation will not be affected. The pedal equation represents, therefore, a system of curves in general which have the same size and shape; the positions of those curves are different but are such that one curve can be made to coincide with another by rotating it through a certain angle about the pole. With equation (1), however, the size of the curve—defined in this case by the radius,—is indefinite. To define a particular curve with the help of a pedal equation, it is necessary to add one more relation which would specify the position of the curve in general, and in cases like (1), the size.

Since

$$\frac{1}{p^2} = u^2 + \left(\frac{du}{d\theta} \right)^2, \quad u = \frac{1}{r} \quad (7)$$

it follows that the p - r equation gives in reality a differential equation of the first order in polar coordinates. Thus it is not surprising that instead of a single curve this type of equation represents a system of curves, each curve of the system corresponding to a particular value of the arbitrary constant of integration.

3. When the system of curves mentioned above possesses an envelope, we shall have the p - r coordinates of any point of the envelope the same as those of one of the curves at the corresponding point of ultimate intersection. Therefore, the coordinates of the envelope must also satisfy the given pedal equation; that is to say, the envelope is also represented by the pedal equation.

For example, the straight lines given by $p=a$, have the circle $r=a$ as their envelope. So the pedal equation

$$p=a \quad (8)$$

should represent the circle also. [*Cf.* equations (2)].

As another illustration let us take the equation

$$a p = r^2. \quad (9)$$

The system of circles represented by this equation clearly has the circle $r=a$ as the envelope, which must, therefore, be included amongst the curves that the equation (9) should represent.

For a point of ultimate intersection, that is, a point on the envelope, u must have equal values, and so $\frac{du}{d\theta}$ must vanish. This indicates that the point of ultimate intersection on a curve, if it exists, must be such that the radius vector is the normal there. For this point

$$\frac{1}{p^2} = u^2 \text{ only,} \quad (10)$$

$$\text{or, } p=r.$$

And as the system of the curves is obtained here by rotating one of them about the pole, the different points of ultimate intersection would be obtained by rotating one such point about the

pole. Hence their locus, that is the envelope of the system, is a circle with the pole as the centre.

Therefore, every pedal equation should represent such a circle in addition to the usual curves, provided that one of the latter can have one or more normals drawn to it from the pole. The radius of this circle would be the length of this normal, and can be obtained from the given pedal equation by putting $p=r$.

4. It might be of interest to note the following simple cases of the familiar pedal equations and the circles they should represent:—

Pedal Equation	The ordinary curve represented by it	The circle which it should also represent
(i) $p=a$	straight line	$r=a$
(ii) $2ap=r^2$	circle of radius a , the pole being on the circumference	$r=2a$ and $r=0$
(iii) $p^2=ar$	parabola	$r=a$
(iv) $\frac{a^2(1-e^2)}{p^2} = \frac{2a}{r} - 1$	ellipse	$r=a(1-e)$ and $r=a(1+e)$
(v) $\frac{a^2b^2}{p^2} = a^2 + b^2 - r^2$	ellipse	$r=a$ and $r=b$
(vi) $\frac{a^2b^2}{p^2} = b^2 - a^2 + r^2$	hyperbola	$r=a$
(vii) $p^2a=r^3$	cardioid	$r=a$ and $r=0$
(viii) $pa^2=r^3$	lemniscate	$r=a$ and $r=0$
(ix) $p=r \sin \alpha$	equiangular spiral	None
(x) $pa^m=r^{m+1}$	$r^m = a^m \sin m\theta$	$r=a$ and $r=0$
(xi) $3p^2+r^2=a^2$	astroid	$r=\frac{1}{2}a$

5. In text-books of Mechanics occur discussions about the stability of circular orbits under any central force which is a function of the distance from the centre. It is presumed that such a circular orbit is possible, at least mathematically; else there would be no point in discussing an untenable problem.

The differential equation of a central orbit in $p-r$ coordinates is

$$\frac{h^2}{p^3} \frac{dp}{dr} = F, \quad (11)$$

and the solution of this is the pedal equation of the orbit. The previous arguments (*Cf.* sections 2 and 3) show that a circle is also a possible orbit, thus justifying the inclusion of the aforesaid problem in Mechanics.

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PROBLEM OF THE TRUE MEASURE OF RELATIVE BAND INTENSITIES

By

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IN measuring relative intensities of bands of a system, various methods are generally used. In this paper we have discussed the merits and demerits of the different methods commonly used and an attempt has been made to test experimentally certain disputable points.

1. RESOLVED BANDS

(a) *Integration method.*—As is well known, a band is emitted as a result of a transition $v' \rightarrow v''$ in an electronic transition $e' \rightarrow e''$ and consists of a number of fine structure lines due to transitions between various rotational levels. The true band intensity is determined by summing up the intensities of all lines in a band. But this kind of investigation involves many difficulties. In the case of a number of band systems, very long exposures are necessary for high resolution, and this involves proportionately long exposures from the standard lamp, for getting the intensity calibration marks. Secondly, where it is a question of determining the intensities of many bands of system, measurements for several thousand lines have to be carried out, and this is an extremely laborious work.

(b) *Single rotation line method.*—Another fairly accurate and far less laborious method is the comparison of intensities of selected fine structure lines in different bands, but having the same rotational quantum numbers. But this method again involves complete resolution of bands with the accompanying difficulties. Also since the rotational energy distribution is dependent on the moment of inertia, which varies slowly with vibration quantum numbers, this method is not entirely free from objections.

2. UNRESOLVED BANDS

(a) *Integration method.*—Many of these difficulties are eliminated if unresolved bands are used for measurements. The optical densities of a large number of points on the contour of a microphotometer record of a sequence of unresolved bands, are calculated. The intensities corresponding to these blackenings are read from the blacking-intensity curves previously prepared for the various bands and a curve is then constructed for each band with intensities as ordinates and wave-lengths as abscissae. The integration of the area under this curve after correction for the energy function of the standard lamp gives a quantity which is proportional to the intensity of the band. Intensities determined by this method are generally referred to as the "total" or "integrated intensities". Alternatively, a slightly different curve with intensities as ordinates and distances along microphotometer record as abscissae, is also employed. The "total" or "integrated intensities" of bands can also be calculated with the help of these second type of curves. But in this case, a correction for the dispersion of the spectrograph used has to be applied.

This method, however, cannot be satisfactorily applied where bands overlap the fine structure of the preceding bands, or where foreign disturbing lines are present within the bands. In such cases the intensities of disturbing lines cannot be effectively eliminated on account of the difficulties of correct extrapolation.

(b) *Method of "Peak" or "Head" Intensities.*—The point of maximum intensity in an unresolved band is in many cases fairly close to the band-head. Ornstein and Brinkman ⁽¹⁾ have shown by elaborate experiments on violet CN system in arc, that this point of maximum intensity near the head, represents almost the true intensity of a band. This they verified by photographing the bands on a prism instrument as well as on a concave grating, *i.e.*, employing both unresolved as well as resolved bands. Taking the moment of inertia of the molecule to vary only slightly with vibrational quantum number, the band head will occur in every case at nearly the same *J* value, and then the 'band-head intensity' or the 'peak intensity' will be approximately proportional to the total intensity of the band.

Experimentally these 'peak intensities' can be determined with comparative cases. It is also possible to eliminate the

disturbing effects of the structure of the preceding bands or foreign lines with a fair amount of precision.

It is on account of its easy nature that many workers have employed the 'peak intensity' method. Johnson and Tawde⁽²⁾ and Tawde⁽³⁾ have used this method for investigating the relative band intensities of the C_2 (Swan) and N_2 second positive systems respectively. Langstroth⁽⁴⁾ in testing his excitation theory has also used the same method. He has, however, attempted to show that the 'peak intensities' are proportional to the 'total intensities' by measuring the intensities of a few bands of the N_2 second positive system by both methods. This evidence about the proportionality between the 'peak intensities' and the 'total' or 'integrated intensities' cannot be said to be wholly conclusive. Langstroth has examined only four bands of the N_2 second positive system, whereas the whole system consists of about 49 bands extending over a wide spectral region. For testing the general validity of Langstroth's assumptions, the bands examined must be separated by a wide margin of vibrational energy.

It is with the idea of deciding this point that we utilize in this paper, the experimental results of another investigation aimed at altogether a different problem. The system which forms the subject of this investigation is the nitrogen second positive system produced in a low temperature discharge tube source.

RESULTS

The nitrogen second positive system was excited in a discharge tube of the usual H-type fitted with aluminium electrodes. The tube containing the two electrodes was 25 cm. long and had diameter of 7 mm. Two small bulbs containing P_2O_5 and KOH were attached to the discharge tube to remove any water vapour or carbon dioxide present in the tube.

The pressure of the air inside the tube was 1.2 mm. The tube was run by an induction coil giving a high frequency voltage. The primary voltage was 10 volts and with it the current in the secondary was 1.0 milliamps. No condenser or spark gap was used in the circuit.

The bands were examined end-on through the quartz window of the discharge tube. The intensity measurement technique followed by us has been described in detail by Read and Johnson⁽⁵⁾, Johnson and Tawde⁽²⁾, Elliot and Cameron⁽⁶⁾ and others.

In the following table No. I, we give the ratios of intensity both by integration and peak procedures.

We call I_i the integrated intensity of unresolved band, and I_p the peak intensity of the same. The ratio I_i/I_p will be designated as ρ . It is given in the 3rd column of the table No. I below :

TABLE No. I

Ratios of the Integrated to Peak Intensities

Band (v' , v'')	Wave-length	Ratio $\frac{I_i}{I_p} = \rho$
1,6	4574 A.U.	1.15
2,7	0.99
3,8	0.86
0,4	4344 A.U.	1.59
1,5	1.49
2,6	1.25
3,7	1.11
4,8	0.77
0,3	4059 A.U.	1.37
1,4	1.31
2,5	1.10
3,6	1.12
4,7	0.91
0,2	3805 A.U.	1.18
1,3	1.05
2,4	1.05
3,5	0.95
4,6	1.04
0,1	3577 A.U.	1.00
1,2	0.96
2,3	0.82
0,0	3371 A.U.	1.00
1,1	0.91
2,2	0.87
3,3	0.85
4,4	0.80
1,0	3159 A.U.	0.84
2,1	1.00
3,2	0.82
4,3	0.77
2,0	2977 A.U.	0.69
3,1	0.61
4,2	0.64

DISCUSSION AND CONCLUSIONS

Since the problem under discussion refers to intensity values on a relative scale, the study of comparison has become a much easier matter. In any one condition of excitation, the actual

intensity of the individual bands should bear a definite relation with each other, so that the intensity distribution obtained for that excitation condition by the peak method should bear a constant ratio with that obtained by the integrated intensity method, if both of these procedures are to be preferred for investigation of band intensities. For the sake of easy comparison, we can reduce this ratio to unity by choosing 1000 as the unit for the (0, 0) band in each case. If the relative scale of peak values is to compare favourably with that of the integrated ones, the ratio ρ of column 3 (Table No. I) should for each band compare favourably with unity within the limits of experimental errors. Glancing along the column 3, we find that the agreement is particularly good on the higher wave length side of the (0, 0) band, but on the lower wave length side, of the (0, 0) band, there is comparatively a large departure from unity in the value of ρ . This means that in the latter region, the peak values are over-estimated or the integrated ones under-estimated. We are inclined to believe in the former possibility. In the following paragraphs, an attempt will be made to justify this belief.

The intensity technique applied here assumes the non-resolution of bands. A band is said to be unresolved if it appears as part of a continuous spectrum. This occurs on perfect overlapping or mixing of rotational structure. If this condition is not satisfied in practice, it may result in giving a wrong estimate of intensity both by integration and peak methods. With increasing dispersion, it may happen that the structure lines are resolved. Dispersion being not the same for the entire spectral region investigated, some bands of the system may be resolved and others not. Where they are resolved, error might occur in the estimation of intensities, as the appearance of the structure lines is against the basic assumptions of the methods adopted. In this particular case, we were satisfied that no mistake on this account occurred as the slit of the spectrograph was adjusted to proper limits and confirmation as to the absence of structure in any of the bands was also obtained from the microphotometer records. Having ruled out the likely source of error pointed out above, we have to seek the reasons for lower ratios in the region of lower wave lengths. It is not likely that there could be an over-estimate or under-estimate of intensity by integration procedure as long as the overlapping of adjacent bands, if any, can be successfully accounted for. In this particular case, it was practically absent and where present to some small extent in a few

cases, it raised no serious difficulties in making the necessary corrections. The low magnitude of ratio ρ in the region of lower wave lengths may, therefore, be a consequence of over-estimates in the peak values.

The elementary considerations of band spectroscopic theory indicate that the relative intensities of bands of a system, as calculated by 'single rotation line' method, are correct, if the lines selected from the various bands have the same J value. Similarly in computing relative intensities of unresolved bands by 'peak intensity' method, correct values will be obtained if the peak or head occurs at nearly the same J value in each band. This would happen provided the moment of inertia changes but little with vibrational quantum number⁽⁷⁾. As a matter of fact, this assumption cannot be taken to be strictly valid in all cases. We find that for the two electronic levels involved in the second positive system of nitrogen, a relatively large-change in the moment of inertia takes place with change in the vibrational quantum number. Making use of the formula⁽⁷⁾ with which the J value for the head can be calculated, and the necessary constants⁽⁸⁾ given in Jevons' Report on Band Spectra, we get the values for the system under discussion. These values are given in table No. II. Thus we see from the table that in the region of lower wave length, (*i.e.*, the region of (0, 0), (1, 0) and (2, 0) bands), there is a relatively large change in the J value at which the peak or head is formed. This would cause in the region of lower wave-lengths, a much higher value for the intensity by the peak method than would be obtainable otherwise under conditions of the same J value.

TABLE No. II

Band	J value for head
1,6	6
0,4	7
0,3	7
0,2	8
0,1	9
0,0	11
1,0	13
2,0	17

If the above contention is accepted, it explains why the ratios of integrated intensity to peak intensity entered in

column 3 of table No. I show fluctuations with wave lengths. From the (1, 6) band to (0, 0) band, the J value for the head shows only slight increase (see table No. II). The peak values registered in this region will, therefore, be very nearly correct. Hence the ratio ρ should be very nearly equal to one, and should show only a gradual decrease as we approach shorter wavelengths. This is borne out generally by our results entered in table No. I, except in a few cases where on account of the small value of the intensity, the percentage error is likely to be great. But from the (0, 0) band to (2, 0) band the J value for the head increases considerably (see table No. II), and this results, as expected, in a sudden decrease in the value of the ratio from 1.00 to 0.64.

The gradual decrease in the value of the ratio observed within the various sequences can also be similarly explained. In each sequence, the J value for the head increases as we go in the directions of higher to lower wave lengths.

Thus on account of the imperfections involved in the assumptions made regarding peak intensities, we are inclined to place more reliance on the values derived from the integration method. The conclusion, therefore, that the peak intensities are generally proportional to the integrated or total band intensities, has to be taken with certain reservations.

For rigorous test of theoretical aspects, it is an ideal thing to be in possession of accurate data, such as that of integrated intensities. But where the integration method is very laborious or is not practicable for any particular band system, peak intensity is the nearest approximation to true band intensity that one could have. It is the simplest to compute and far less laborious, especially for a system extending over a large wave length region.

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DIPOLE MOMENT AND MOLECULAR STRUCTURE OF HIGHER FATTY ACIDS

By

G. R. PARANJPE AND P. Y. DESHPANDE

DIPOLE moments of first few members of the fatty acid series are already investigated by different authors. The results obtained, however, are rather discordant and diverging. This is not surprising, for the first two or three members of any homologous series are generally known to behave abnormally. It was, therefore, decided to investigate the higher members for their dipole moments. These fatty acids associate to form dimers, *i.e.*, two molecules associating end to end with their active (COOH) groups together. The values of dipole moments are utilized to suggest a structural configuration of the associated carboxyl group.

The choice of lauric acid, myristic acid and palmitic acid for these investigations was mainly based on the fact that considerable X-ray and other data are available in the literature. Trilaurin and palmitone were studied to compare and verify the results obtained for the three acids.

The solution method, as introduced by Debye and used in these investigations, has been subjected to reconsideration in order to account for the solvent effect. Since, however, most comparisons have been based upon measurements in the same solvent or in solvents differing by no great amount in dielectric constant, few, if any, of the accepted conclusions as to the dielectric properties of various substances can be regarded as invalidated by the recent development of the solvent effect considerations.¹⁸

All the substances are solids at room temperature. An extra pure variety of each of these substances was obtained from Messrs. Schering Kahlbaum. All the experiments were carried out at room temperature which was about 30°C. The three acids belong to the acetic acid group having the general formula

$C_n H_{2n} O_2$. The organic acids are characterised by the atomic group $COOH$ called the carboxyl group and contain a normal carbon chain.

Benzene was used as the solvent. A sample of benzene as obtained from Messrs. Schering Kahlbaum was guaranteed free from thiophene. It was first distilled and recrystallised. The solid residue obtained by decantation was allowed to stand over sodium wire. Fresh sample was used every time thus avoiding the use of stored sample.

The densities of the solutions were determined by means of specific gravity bottles of 50 c.c. capacity. As all the substances are sparingly soluble in benzene, the density of the solution differed from that of benzene by only a small amount. Hence it was desirable to use bottles of large capacity to minimise the errors in weighing. All care was taken to ensure correct weighings and the usual procedure regarding the calibration of weights, etc., was gone through. The use of benzene as the solvent necessitated a great deal of care while taking observations. It has a high coefficient of expansion. Consequently, hand contact with the specific gravity bottle had to be avoided. Due to its volatile nature some time was always allowed before weighing the bottle to allow it to come to the room temperature. A correction for the quantity of benzene evaporating during this interval was made by determining the diameters of the bore of the capillary in the glass stoppers and noting the height of the liquid in the capillary. The correction became small enough as the concentration increased. The concentrations are expressed in terms of mole-fractions.

The refractive index was determined for the sodium D-line by using the Abbé auto-collimating Refractometer. The solution used was the one for which the mole fraction and the density were previously determined. The same solution was used for the determination of the dielectric constant also. Hence all data about the mole fraction, the density, the refractive index and the dielectric constant were known at the same time and for the same solution thus avoiding the graphical interpolations.

Measurements of dielectric constants of the different solutions were carried out at 7,500 Kc. A compensation circuit was used to detect and to rectify the incoming high frequency oscillations. The resonance was observed by putting in the plate circuit a sensitive galvanometer and noting the maximum change in the plate current of the valve. Brown⁸ recommends

this method as it is easily manipulated and permits rapid determination of small capacities. The oscillator had an output of 2 watts. It was fed entirely on independent batteries thus ensuring stability. Its direct interaction on the detecting circuit was avoided by separating them by a distance of about 5 meters. The filament current shown by a milliammeter in the circuit was controlled by a variable resistance to avoid any fluctuations in the plate circuit. A precision dial mounted on the tuning condenser greatly improved the setting of the wavelength emitted by the oscillator. The oscillator showed great stability at certain frequencies. From these a frequency of 7,500 Kc. (40 m) was selected for regular work. This frequency was checked from time to time.

The valve volt-meter used to observe resonance was the same as was used by the authors¹¹ in their investigations of the dielectric properties of some vegetable oils.

The test condenser was prepared of two thick (0.45 mm.) silver plates bent cylindrically. They were then fixed between the two walls of a Dewar's flask which was cut at its base and inverted. The diameters of the cylindrical silver plates were so adjusted that the plates were kept in position in the Dewar's flask by the forces due to their elasticity and the use of solid supports was avoided. Leads were joined to small extensions of the silver plates which were bent at right angles. This avoided the contact of baser metals with the solution inside the condenser. The outer plate was earthed. To avoid any stray capacity effects the test condenser was completely screened, the screen being earthed. A cell so constructed approximates closely to an absolute condenser, i.e., a condenser in which the capacity is strictly proportionate to the dielectric constant of the medium between the plates. It also satisfied the conditions laid down by Hartshorn and Oliver⁶ for the reliable determination of the dielectric constant. The dielectric constant was then determined by the usual procedure.

Having thus determined all the necessary data, the value of $P_{1,2}$ the total polarisation of the solution was determined by the equation :

$$P_{1,2} = P_1 + (P_2 - P_1)f_2$$

while P_2 the polarization of the solute was calculated by the equation :

$$P_2 = \frac{P_{1,2} - P_1 f_1}{f_2}$$

f_1 and f_2 being the mole fractions of the solvent and the solute respectively. The value of P_2 at infinite dilution was then determined by plotting P_2 against f_2 and extrapolating the graph to $f_2=0$. The value ∞P_2 was also determined by using the equations suggested by Hedestrand.⁷ A comparison between the values obtained by the extrapolation of the graphs and those obtained by the Hedestrand's method shows a close agreement. It may, therefore, be concluded that the conditions contemplated by Hedestrand in obtaining the value of ∞P_2 by his equation are also realised satisfactorily in extrapolating the $P_2 f_2$ graph to infinite dilution.

Sugden²¹ has suggested another method of arriving at the proper value of ∞P_2 . He supposes that the permanent molecular dipole in a solution may be regarded as surrounded by an 'atmosphere' of dipoles of opposite signs, produced partly by induction in the polarizable solvent molecules and partly by orientation of adjacent permanent dipoles. The measured polarization, therefore, appears to be less than the true value. He then suggests that the correction for the opposing atmosphere of dipoles should be a function of the volume polarizability of the solution and that the true value of ∞P_2 should be obtained by extrapolating the graph of P_2 against the volume polarizability

to $\frac{\epsilon-1}{\epsilon+2}=0$, i.e., $\epsilon=1$. The idea is that, since $\epsilon=1$ holds good for

gases, the extrapolated value of ∞P_2 would be the value for a molecule which would be as free as it would be in gaseous state under low pressure. However, so far as the solution method is concerned, this idea could hardly be materialised. When a dipole is transferred from a gas, at not too high a temperature, into a solution in a nonpolar solvent, it is transferred from an environment which, to a first approximation, is non-polarizable, into a position where it is surrounded by polarizable molecules. Under these conditions it becomes necessary to examine the mutual effects of the dipoles and the solvent molecules. It would be, therefore, reasonable to extrapolate the $[P_2 \text{ against } (\epsilon-1)/(\epsilon+2)]$ graph upto $(\epsilon-1)/(\epsilon+2)=(\epsilon_1-1)/(\epsilon_1+2)$, i.e., when $\epsilon=\epsilon_1$, the dielectric constant of the solvent. The values of ∞P_2 obtained in this way are in close agreement with those obtained by the other two methods. The advantage of Sugden's method is that the graph is a straight line. Extrapolation, therefore, is not likely to involve any error. For comparison, the values of ∞P_2 obtained by these three methods are given in the following table :—

TABLE 1

	Method of Extrapolation	Hedestrand's Method	Sugden's Method
Lauric acid	79.5	80.098	82.8
Myristic acid	88.9	88.320	89.8
Palmitic acid	98.9	98.535	100.6
Trilaurin	352.9	353.040	353.5
Palmitone	261.5	263.450	275.0

When P_2 is plotted against f_2 , the values of P_2 decrease with increasing concentration. The decrease is prominent in the case of trilaurin and palmitone, which have greater moments than those of the three acids. Many organic compounds are known to associate at ordinary temperatures, both in solution in non-polar solvents and in the gaseous state.²⁵ The literature gives ample evidence in favour of association due to dimer formation. (8, 10, 20, 24) The decrease of P_2 with increasing concentration may, therefore, be interpreted to show more and more single molecules pairing to form dimers as the concentration increases. Benzene is somewhat a dissociating solvent and the general conception is that the degree of association of fatty acids in benzene solution decreases with molecular weight. This general conception is also confirmed by Smith.¹⁶

The electronic polarization was determined from the refractive index measurements. It is given by the equation:—

$$P_E + P_A = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

When P_{E_2} f_2 is plotted against f_2 , a straight line is obtained in each case. This linearity is further confirmed by the calculations by least square method which in all cases give the correlation coefficient practically equal to one. The linear nature of these graphs shows the constancy of P_{E_2} throughout the concentration range studied in these experiments. This is only an evidence of the fact that the effect of molecules upon the refractions of neighbouring molecules is negligible. The value of P_{E_2} at infinite dilution was then found out by extrapolation.

The contribution to molar refraction by differently situated electrons in a molecule is calculated by Smyth¹⁹ by using simple equations used by von Steiger²⁶ to calculate bond refractions from atomic refractions. By using these values for bond

refractions for the different electronic systems in each atomic group, the molar refractions for all the substances were calculated and were found to be in close agreement with those obtained by the extrapolation method.

As the molecule is large and its moment small, it was necessary to take into account the atomic polarization also. A survey of the existing literature shows that all attempts to account for the atomic polarization have so far failed.¹⁷ Sugden²² remarks "there is no clear relationship that can be traced between the dipole moments and P_A nor can P_A values be allotted to groups. So far as the use of P_A values in calculating dipole moments is concerned, the practice of Zahn and others of taking P_A as 10 per cent of P_E is probably correct and gives negligible error." Wolf²⁰ and Smith¹⁸ have assumed, however, the value of P_A for the fatty acids to be 15 per cent of P_E . This is higher than that desired by Zahn and others but apparently necessary in view of the greater sizes of the molecules. Consequently, in these calculations P_A is assumed to be 15 per cent of P_E and is allowed for. The values of electric moments for the substances investigated are shown in table No. 3. Values "uncorrected" are obtained by not taking into consideration the atomic polarization while those "corrected" are obtained after deducting P_A (*i.e.*, 15% of P_E). The values of ∞P_2 , ∞P_{E_2} , P_A etc. are collectively shown in table No. 2 :—

TABLE 2
Final Results for all the Substances

Substance	Molecular Polarization, ∞P_2	Electronic Polarization, ∞P_{E_2}	Atomic Polarization, P_A	Orientation Polarization, P_O	Electric Moment, (corrected) $\mu \times 10^{-18}$
Lauric acid	79.5	59.19	8.88	11.43	0.75
Myristic acid	88.9	66.72	10.08	12.10	0.77
Palmitic acid	98.9	75.24	11.28	12.38	0.77
Trilaurin	352.9	187.60	28.13	137.27	2.59
Palmitone	261.5	147.60	22.14	91.76	2.12

TABLE 3

Values of Dipole Moments ($\times 10^{-18}$)

Substance	Uncorrected	Corrected
Lauric acid	1.02	0.75
Myristic acid	1.04	0.77
Palmitic acid	1.07	0.77
Trilaurin	2.84	2.59
Palmitove	2.39	2.12

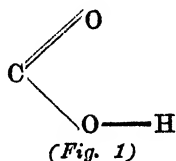
The difference between the uncorrected and the corrected is quite significant. For comparison, the values of electric moments as obtained by different workers are collected in table no. 4. In view of these values, the values for the dipole moments of the three acids calculated without considering the atomic polarization are positively higher and misleading. The values obtained after deducting the atomic polarization are in good agreement with those obtained by Smith.¹⁶ Comparing these values with those found by Wolf²⁹ who has worked practically under the same conditions, it would appear that the length of the carbon chain has little effect on the moment of the molecule. Wilson & Wenzke²⁸ have also arrived at the same conclusion.

After all these considerations, values of moments for the three acids (corrected) can hardly be supposed to be zero. Smyth and Rogers²⁰ have supposed the moment of the double molecules of acetic acid to be zero and Ebert, in a private communication to Smyth has confirmed this. Ebert obtained $P_g = 18.85$ for acetic acid in benzene and P_{E_2} for solid acetic acid at 0°C equal to 19.4 . On the other hand, Zahn³¹ has obtained 0.99×10^{-18} as moment of the double molecule of formic acid. The results for double molecules obtained by Wolf,²⁹ Smith¹⁶ and others, quoted before, give constant values. As these are obtained practically under the same conditions as those obtained in these investigations, they confirm that the double molecules of the higher fatty acids at least have moments which cannot be considered as zero. In other words, the association does not completely neutralize the moments of the individual molecules.

TABLE 4
*Comparative Values of Dipole Moments obtained
 by different Authors*

	Formic acid	Acetic acid	Propionic acid	n-Butyric acid	Iso-Valeric	Stearic acid	Lauroic acid	Myristic acid	Palmitic acid
(29) Wolf (§) in benzene solution.	1.19	0.74	0.63	0.68	0.63	—	—	—	—
(20) Smyth & Rogers, in ether solution.	—	1.4 (*)	—	—	—	—	—	—	—
(31) Zahn, in gaseous state.	1.51(*) 0.99 (+)	1.73 (*)	1.74 (*)	—	—	—	—	—	—
(2) Briegleb in benzene solution(+).	1.45	1.04	0.88	0.93	0.89	—	—	—	—
(28) Wilson & Wenzke, in dioxene solution.	2.07 (*)	1.74 (*)	1.75 (*)	—	—	1.74 (*)	—	—	—
(16) Smith (+) in benzene solution.	—	—	—	—	—	—	—	0.76	0.72
Authors (+) in benzene solution.	—	—	—	—	—	—	0.75	0.77	0.77

The structural formulæ for the three acids show that they are all saturated. The chains neither contain any double bond nor any OH group which are polar. Each of them, however, possesses at its end the characteristic COOH group which is responsible for the electrical dissymmetry of the molecule giving rise to an electric moment. Its structure is generally represented by :—



which contains both the double bond and the OH group. Both

- (§) Association effects are ignored ;
- (+) Dimer or double molecule ;
- (*) Single molecule.

of these are polar in character and, therefore, contribute to the electric moment. In the case of palmitone the dipole resides in the ketone group $C=O$ only, the two carbon chains on both the sides of this group containing no group polar in character. Trilaurin contains three lauric acid residues and hence three hydro-carbon chains. The glycerol portion at the end of the molecule forms the polar group and the three chains lie parallel to one another.

J. J. Thomson²³ has shown that moments of molecules may be calculated, in certain cases, on the assumption that it is the vector sum of the individual moments characteristic of certain groups. Following this suggestion, Williams²⁷ calculated the moments contributed by a number of groups on the assumption that the benzene ring residue itself is non-polar. He found the $COOH$ group to have the moment 0.9×10^{-18} . This appears to be too low as compared to 1.51×10^{-18} for the single molecule of formic acid² and to 1.4×10^{-18} for that of acetic acid.²⁸

Eucken and Meyer⁴ have adopted another method. They assign a definite moment to a bond or linkage rather than to a group. These moments are then used on the assumption that the carbon valences in single bonds in aliphatic compounds make the tetrahedral angles of 110° with one another and that the two valences of oxygen also make an angle of 110° with each other. It is found that in spite of certain limitations imposed on this method, it has yielded valuable information about the dipole moment and the structure of the molecule.

The structure of the carboxyl group in the associated state has attracted much attention. Consequently, several studies have been made. Pauling and Brockway¹² give a plane structure which was obtained in the case of formic acid by electron diffraction method. In this structure the $C-O$ distance is $1.29 \pm 0.05 \text{ \AA}$, and the $O-C-O$ angle is $124^\circ \pm 3^\circ$. Zachariasen³⁰ has determined the configuration to give the $O-C-O$ angle as of 126° . Latimer and Rodebush⁹ agree with Pauling and Brockway. Zahn suggests another model. Taking into consideration the relative sizes of the C and O atoms and assuming the tetrahedral symmetry of the carbon atom, he thinks it almost possible, geometrically, to fit the molecules together in such way that the four O atoms lie in the corners of a square and the C atoms on a line perpendicular to the square. The sizes of the atoms permit of a distortion of the square by interaction between the $O-H$ and the $C=O$ groups such that, the planes of the two molecules subtend an angle a little less

than 120° . Using the method of Eucken and Meyer⁴, Zahn then calculated 1.1×10^{-18} as the value of the electric moment of the double molecule of formic acid. This compared favourably with 0.99×10^{-18} which he obtained experimentally. Pauling and Brockway, however, state that this model does not agree with theirs. Gillette and Sherman⁵ have excluded Zahn's model while considering the hydrogen bond in the association in carboxylic acids. Zahn himself calls his model as only tentative²². The model of Pauling and Brockway is a symmetrical one and, therefore, possesses no moment. As the double molecule of the higher fatty acids shows a significant moment of about 0.7×10^{-18} , the plane symmetrical structure may not be possible in the case of higher fatty acids. The possibility of a different type of mechanism in the association of the double molecules of the higher members of the fatty acids is also hinted at by some.

Taking into consideration the chemistry of the molecule and the value of its dipole moment, it is to be suggested that a space-structure, rather than a plane one, represents the state of association more satisfactorily. In this structure the O—C—O angle is of 125° as suggested by Pauling and Brockway¹² and by Zachariassen.³⁰ The hydrogen is supposed to have the covalency maximum of 2. Sidgwick¹⁸ asserts that whatever may be the exact mechanism of the coordinated hydrogen its occurrence is beyond doubt and that, on the chemical side, there is no reason to doubt this. When such a coordination of hydrogen between two oxygen atoms takes place the angle O—H—O becomes 180° . The three atoms therefore lie in a straight line. The recognition of the fact that the valency angle in coordinated hydrogen is 180° has removed the difficulty of formulating the dimeric molecules of the hydroxylic acids. Moreover, realising that the covalencies of the hydrogen atom are in one straight line, it is evident that the symmetrical situation of the two hydrogen atoms in the double molecule will not increase the strain in the molecule.

The two O—C—O planes, however, instead of being in the plane formed by the four O and the two H atoms, are each inclined to the latter at an angle of 135° , thus making the C—O—H angle equal to 110° , the usually accepted value for the oxygen valency angle. The mutual inclination of the two O—C—O planes is obviously equal to 90° .

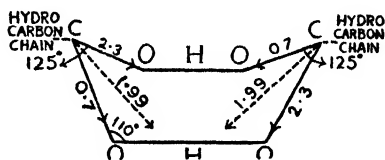
Both theory and experiment show, that in the type of hydrogen bond formation common in organic compounds, there

is not usually complete degeneracy, the hydroxyl (OH) and the ketone (C=O) groups still preserving their individual characteristics.¹

Sidgwick¹⁴ further asserts, that in the case of coordinated hydrogen in chelate formation, it is not to be supposed, that one of the oxygen atoms has permanently a different relation to the hydrogen from the other. Gillette and Sherman⁵ have arrived at the conclusion that the coordinate hydrogen is definitely polar in character. It is reasonable to suppose, therefore, that if the two oxygen atoms are similarly related to the coordinate hydrogen atom and if the coordinated hydrogen is polar in character, then, the coordinated hydrogen bond may be as polar as the ordinary O—H bond. In fact, Sidgwick¹⁵ has pointed out that the dipole moment of the link between hydrogen and the atom to which it is attached is fairly large in most substances that form hydrogen bonds. He gives 1.6×10^{-18} as the value of the H—O bond. This is just the value of the ordinary O—H link as given by Eucken and Meyer.⁴ On the strength of this evidence about the polar character of the coordinate hydrogen bond, it may be supposed that the two H—O moments, being equal and opposite, cancel each other. The only effective moments remaining in the molecule are, then, the two C=O and the two C—O moments. Accepting the values given by Eucken and Meyer for these bonds, the pair C=O and C—O on one side will have a resultant given by:—

$$R_1 = \left\{ \begin{array}{l} \text{Resultant mom-} \\ \text{ent of C—O} \\ \text{and C=O bond} \\ \text{moments} \end{array} \right\} = \sqrt{(2.3)^2 + (0.7)^2 + 2(2.3)(0.7) \cos 125^\circ} = 1.99$$

since, the carbon valency angle, that is, the angle between these two bond moments is 125° . The same pair on the other side and belonging to the other molecule associating with the first, will also have a resultant of 1.99.



(Fig. 2)

In the associated state of two molecules, therefore, we have two moments of equal magnitude acting at such an angle that the resultant moment of the associated molecule is 0.78 as determined by actual observations in these investigations. This angle can be determined as follows. If the angle between

the two moments is denoted by θ , the resultant 0.78 will be given by:—

$$0.78 = \sqrt{(1.99)^2 + (1.99)^2 + 2(1.99)(1.99) \cos \theta}$$

which gives the value of θ as 117° . Assuming this angle between the two resultants and working backwards, the model as already described is easily obtained.

The value 117° of the angle obtained as above gives a proof in favour of 0.78 as the value of the moment. For, this angle leads to a structure which involves the values of the valency angle of carbon and oxygen as are already generally accepted. The structure, therefore, has no strain which explains the stability of the molecule. Meyer has calculated that no sufficient rotation in the molecule will take place unless the temperature is raised to $20,000^\circ\text{C}$. The whole structure is thus in conformity with all the existing data and in addition gives the proper value for its moment. Hence, the model suggested here may be supposed to represent truly the state of association when two molecules of the higher fatty acids join together to form a dimer.

The data in the case of trilaurin and palmitone is rather scanty. Hence, no definite interpretation can be placed on it. These two substances, however, help to check the results obtained in the case of the three acids. In palmitone, the polarity of the molecule is all due to the characteristic ketone ($\text{C}=\text{O}$) group, the rest of the chain containing no polar group. Neither the length of the chain nor the position of the ketone group in the chain has any effect on the polarity of the molecule as a whole. Wolf has considered that the oxygen may be combined with the carbon by an ordinary double bond, with the $\text{C}=\text{O}$ group alone all important in determining the moment, the attached groups having only secondary or no influences. After examining a large number of ketones, he concluded that the valence angle in the aliphatic ketones is not necessarily distorted from 110° . Saville and Shearer in an X-ray investigation of higher aliphatic ketones, have found that, in the solid state, the two hydrogen carbon branches on either side of the $\text{C}=\text{C}$ group are in the same straight line which suggests the usual tetrahedral angle of 110° for the valences of the carbonyl group. After making a survey of all the available data on ketones, Smyth comes to the conclusion that, it is reasonable to suppose that, the moment of a ketone molecule is inherent in the carbonyl group and that,

the angle between the attached chains has but little effect upon the moment. The value for the moment of the palmitone molecule is in good agreement with those for other ketone compounds.

Looking to the structure of the trilaurin molecule, it would be expected that, the value for its moment cannot be exactly equal to thrice the moment of lauric acid, which for the single molecule, may be taken as 1.4. It would be noted that, in the first and third line, in the structure of trilaurin, the H in the COOH group is replaced by CH_2 while, in the second line it is replaced by CH. This replacement lowers the value of the moment. The C-C bond is nonpolar and, therefore, though introduced in the molecule, does not contribute to the moment of the molecule. Hence, the value obtained is lower than three times that for the single molecule. The association is also responsible for lowering the moment to some extent.

One of us (P. Y. D.) desires to express his gratitude to the University of Bombay for giving a grant towards the expenses incurred in carrying out these experiments.

SUMMARY

The dipole moments of lauric, myristic, and palmitic acids, trilaurin and palmitone are determined at room temperature by dissolving them in benzene. Assuming the atomic polarization to be 15% of the electronic polarization, the values for the moments are 0.75×10^{-18} , 0.77×10^{-18} , 0.77×10^{-18} , 2.59×10^{-18} , and 2.12×10^{-18} respectively. In the case of the acids these values are for the moments of molecules in the dimeric form. The existing data regarding the structure of the associated carboxyl group in the dimeric molecule is discussed and in consequence a new structure is suggested in the light of the values of the moments. It is shown that, this structure represents more satisfactorily the state of association and is in general conformity with the existing ideas about valence angles, etc.

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THE APPLICATION OF THE ELECTRO-MAGNETIC THEORY OF MIE TO THE MEASUREMENT OF SIZE OF SMALL DROPS

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INTRODUCTION

THE theory of Mie based on the electro-magnetic theory of light has been employed to study the scattering of light by small drops, especially fog particles. The results have been compared with those obtained from the circular disc theory of corona, which is commonly used in the measurement of size of drops. It has been shown that the circular disc theory is much more accurate than was hitherto supposed.

I

The theoretical investigation of the effect of a spherical obstacle too small to cause rainbows on a plane light wave was taken up as soon as the diffraction phenomena established the wave theory of light. The principle of diffraction and Babinet's principle were used in the investigation. The spherical obstacle was assumed to behave as an opaque disc, whose diameter was equal to that of the obstacle and whose axis was parallel to the incident light. The formula derived gave a relation between the angles of minimum intensity of light scattered in the forward direction and the size of drop. The formula becomes less accurate as the angle of scattering becomes larger. Hence, the formula for the smallest angle of minimum intensity

(termed the angle of first minimum) is the most accurate. The formula for the angle first minimum is as follows :—

$$\sin \theta_1 = \frac{3.83\lambda}{2\pi\rho}$$

where θ_1 is the angle of first minimum,

λ is the wavelength of incident light,

and ρ is the radius of the obstacle.

(2) This formula leads to the following conclusions :—

(a) The angle of first minimum depends only on the size and not on the nature of the material of the obstacle.

(b) The scattered light is not polarized.

(c) The angle decreases as the size of the obstacle increases. For large obstacles, the angle is inversely proportional to the radius of the drops.

The numerical results of this formula have been compared with those obtained on the exact theory derived by Mie¹, based on the electro-magnetic theory of light.

Ray² used the less exact formulæ obtained by Love³ and corrected by Rayleigh⁴ to the same purpose, but as will be shown later, his results were vitiated by lack of sufficient numerical data.

II

The formulæ derived by Mie have been given in several papers including the one by the authors⁵. The symbols used in this paper are the same as those in the last mentioned paper.

The intensities of scattered light in various directions in the neighbourhood of the forward direction are given below for several sizes of drops for water (refractive index=4/3) and benzene (refractive index=3/2).

TABLE I

$$\alpha=30. \quad \beta=40.$$

$\pi-\gamma$	I_1	I_2	I_1+I_2
$0^\circ - 0'$	195719	195719	391438
$5^\circ - 6'$	7735	7520	15255
$7^\circ - 15'$	7066	5231	12297
$8^\circ - 7'$	11209	11619	22828
$10^\circ - 0'$	9958	9163	19121

TABLE II

$$\alpha=20. \quad \beta=26.67.$$

$\pi-\gamma$	I_1	I_2	I_1+I_2
0°	45871	45871	91742
$7^\circ - 15'$	2028	1309	3337
$8^\circ - 7'$	419	597	1481
$10^\circ - 0'$	890	1532	2422
$12^\circ - 50'$	4307	4130	8437

TABLE II (A)

$$\alpha=20. \quad \beta=30.$$

$\pi-\gamma$	I_1	I_2	I_1+I_2
0°	42779	42779	85558
$7^\circ - 15'$	2205	2421	4626
$8^\circ - 7'$	694	650	1344
$9^\circ - 56'$	990	409	1399
$12^\circ - 50'$	3088	3171	6259

TABLE III

 $\alpha=12.$ $\beta=16.$

$\pi-\gamma$	I_1	I_2	I_1+I_2
0°	3618	3618	7236
10°	649	576	1225
12° - 50'	323	276	599
15°	342	318	660
18° - 12'	455	440	895
20°	445	448	893
23° - 4'	265	285	550
25°	155	172	327
27° - 7'	82	107	189
30°	94	128	222
35°	201	241	442

TABLE III(A)

 $\alpha=12.$ $\beta=18.$

$\pi-\gamma$	I_1	I_2	I_1+I_2
0°	8415	8415	16830
10°	2044	2479	4523
12° - 50'	589	1004	1593
15°	127	434	561
18° - 12'	240	289	557
20°	311	345	656
21°	391	378	769
25°	530	482	1012
30°	222	275	497
35°	88	62	100

TABLE III(B)

 $\alpha=12$. $\beta=16$, by Rayleigh's formulae.

$\pi-\gamma$	I_1	I_2	I_1+I_2
0°	849	849	1698
$18^\circ - 12'$	281	282	563
$25^\circ - 50'$	130	132	262
$31^\circ - 48'$	164	165	329
$36^\circ - 52'$	180	181	361

TABLE IV

 $\alpha=10$. $\beta=13.33$.

$\pi-\gamma$	I_1	I_2	I_1+I_2
$0^\circ - 0'$	2767	2767	5534
$10^\circ - 0'$	622	650	1272
$12^\circ - 50'$	132	216	348
$15^\circ - 0'$	7	111	118
$18^\circ - 11'$	93	178	271
$20^\circ - 0'$	198	276	474

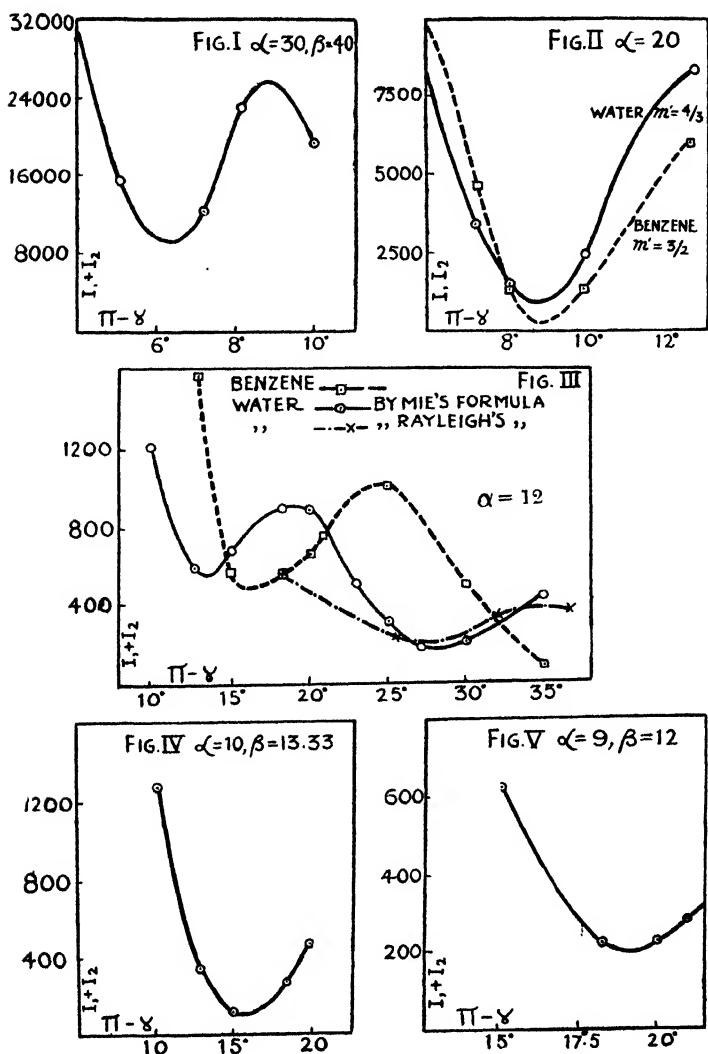
TABLE V

 $\alpha=9$. $\beta=12$.

$\pi-\gamma$	I_1	I_2	I_1+I_2
0°	3466	3466	6932
10°	1256	1402	2658
15°	248	382	630
$18^\circ - 11'$	84	154	238
20°	107	128	235
21	141	147	288

The above results are shown graphically in Figs. 1 to 5.

In figure 3, the value of α is 12.



The angles of the first minimum of total intensity in forward direction for the several drops, as obtained graphically, are given in tabular form in Table VI.

In Table VI:—

*

 $\pi - \gamma_m$ = Angle of first minimum by Mie's theory. $\pi - \gamma_c$ = Angle of first minimum by Circular Disc Theory.

TABLE VI

Nature of Drop	$\pi - \gamma_m$	$\pi - \gamma_c$	Percentage difference = $\frac{\gamma_c - \gamma_m}{\pi - \gamma_c} \times 100$
$\alpha = 30$ $\beta = 40$	6° - 30'	7° - 20'	13
$\alpha = 20$ $\beta = 26.67$	9° - 0'	11°	19
$\alpha = 12$ $\beta = 16$	14° - 0'	18° - 30'	29
$\alpha = 10$ $\beta = 13.3$	16° - 0'	22° - 30'	29
$\alpha = 9$ $\beta = 12$	18° - 0'	25° - 12'	25
$\alpha = 20$ $\beta = 30$	9° - 0'	11°	19
$\alpha = 12$ $\beta = 18$	16° - 30'	18° - 30'	11

In the previous section the theoretical values of the intensity of scattered light in different directions were given. From these values the angles of the first minimum of intensity in the forward direction were graphically estimated in each case.

It is shown in what follows that these angles are really the angles of the first minimum and not a higher order minimum. To show this it is necessary to consider the complex amplitudes of I_1 and I_2 . The terms which go to form these amplitudes for I_1 are given in the Appendix for $\alpha=20$, $\beta=30$ for angles $\pi-\gamma=0^\circ$, $(7^\circ-15')$, $(8^\circ-7')$ and $(9^\circ-56')$. It is noticed from the calculations at the end of each table in the Appendix that the real part of the complex amplitude is small for the smaller values of $\pi-\gamma$. Only for $\pi-\gamma=9^\circ-56'$, the real part is large. For $\pi-\gamma=0^\circ$ the real part is extremely small. It is, therefore, necessary to consider only the imaginary part of the amplitude. To evaluate the imaginary part it is necessary to take into account only 24 terms of the series $\pi_n A_n + \psi_n P_n$.

The value of the imaginary part of $\sum \pi_n A_n + \psi_n P_n$ for $\alpha=20$, $\beta=30$ is

-204.175	for	$\pi-\gamma = 0^\circ$
- 45.768	„ „	$= 7^\circ-15'$
- 21.083	„ „	$= 8^\circ-7'$
22.313	„ „	$= 9^\circ-56'$

In case of $\pi-\gamma=0^\circ$ all the terms of $\pi_n A_n$ and $\psi_n P_n$ are negative. For $\pi-\gamma=(7^\circ-15')$ all the terms of $\pi_n A_n$ and the first 14 terms of $\psi_n P_n$ are negative. The remaining terms for this angle are positive. As the angle $\pi-\gamma$ increases the value and number of the negative terms decreases and that of the positive terms increases; consequently, the nett value of $\sum(\pi_n A_n + \psi_n P_n)$ approaches zero negatively and at a certain angle is zero and then becomes positive and increases. When $\sum(\pi_n A_n + \psi_n P_n)$ is zero the intensity, however, is not zero, as the real part of the amplitude is not zero. It is clear from tables in the Appendix that the values of π_n and ψ_n change gradually and between 0° and $(8^\circ-7')$ the number and value of the positive terms decreases (positive terms in the Tables of π_n and ψ_n in the Appendix give negative terms in the imaginary part of the amplitude of I_1). Thus, the imaginary part of the amplitude of I_1 , decreases steadily as the angle changes from

$\pi - 0^\circ$ to $\pi - (8^\circ - 7')$. Therefore, there will be no minimum between these two angles. The intensity I_2 can be discussed similarly and leads to the same conclusion. Other cases can be similarly considered.

Ray² found that the first minimum for $\alpha=12$, $\beta=16$, on Rayleigh's⁴ theory, is at $\pi - (27^\circ - 30')$ approximately. From the tables and graphs given it is easy to see that this angle is probably the angle of the second minimum. This is all the more probable from the fact that the calculations on Mie's theory give a minimum at $\pi - (27^\circ - 30')$ approximately, but this is the second minimum. Ray had not calculated intensities for angles between $\pi - 0^\circ$ and $\pi - (18^\circ - 12')$; if he had he would have probably found a minimum between these two angles and that too at about $\pi - 14^\circ$ since the angles of the second minimum by the two theories are approximately the same.

An attempt was made to extend Ray's calculations to angles between 180° and $161^\circ - 48'$, in order to test the veracity of this supposition. But, it seems that there are some errors in the values of M_n and N_n published by Ray. (For the significance of the symbols, Ray's paper should be referred). These published values do not give the same values of intensity co-efficients for 0° and 180° as published by Ray.

The intensity co-efficients given by Blumer⁶ for $\alpha=12$, $\beta=16$, on Rayleigh's¹ theory at regular intervals of 10° do not give any new information, as the values given by him are graphically interpolated from Ray's values.

Assuming that there is a minimum of intensity at about $\pi - 14^\circ$ for $\alpha=12$, $\beta=16$ on Rayleigh's theory, it is obvious that the two theories lead to the same value for the angle of the first minimum and this value is not very different from that given by the circular disc theory, namely $18^\circ - 30'$. The circular disc theory is not wholly correct. For instance, it leads to the conclusion that the scattered light is unpolarised if the incident light is unpolarised, which is contrary to experience. Ray's calculations also give in general a smaller amount of polarisation than the calculations on Mie's theory for the same case.

An important conclusion from these results is that the corona method of the measurement of the size of drops is not so defective as it was considered to be by Ray, Wilson and Mecke.⁽⁸⁾ An approximate estimate of the error in the formula

$\sin \theta_1 = \frac{3 \cdot 83 \lambda}{2 \pi \rho}$, θ_1 being the angle of first minimum, is

indicated in the several cases of drops considered. It appears from them that the error (in the case of water drops) decreases as α decreases after 10. The error is maximum for $\alpha=10$. Sufficient data is not available for other liquids to draw conclusions about the variation in the errors in the formula mentioned above.

The authors take great pleasure in thanking Mr. Tamhankar, B.Sc., for his help in checking the calculations.

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APPENDIX

The tables (Ref. 5) in this Appendix give the values of π_n and ψ_n up to $n=27$ for $\gamma=7^\circ-15'$, $8^\circ-7'$ and $9^\circ-56'$ and $\pi_n A_n$ and $\psi_n P_n$ for $\alpha=20$, $\beta=30$, for angles $\pi-\gamma$, $=0^\circ$, $7^\circ-15'$, $8^\circ-7'$ and $9^\circ-56'$.

The terms $\sum \pi_n A_n$ and $\sum \psi_n P_n$ are complex quantities.

In the following tables,

R denotes the real part of $\pi_n A_n$

T " " " $\psi_n P_n$

R' " the imaginary part of $\pi_n A_n$

T' " " " $\psi_n P_n$

Intensity $I_1 = (R+T)^2 + (R'+T')^2$

The values of π_n and ψ_n for 0° are not given as in this case $\pi_n = \psi_n = \frac{1}{2}n(n+1)$ which is a very simple calculation.

The above tables are referred to in the discussion of the results.

$$\gamma = 7^\circ - 15'$$

$$\cos \gamma = \nu = 0.992$$

π_n	n	$\psi_n = \nu \pi_n - 1 - \nu^2 \pi'_n$
1.0000	1	0.9920
2.9760	2	2.9044
5.8805	3	5.5963
9.6434	4	8.8624
14.1734	5	12.4398
19.3599	6	16.0167
25.0753	7	19.2437
31.1773	8	21.7456
37.5121	9	23.1247
43.9172	10	23.0255
50.2250	11	21.0488
56.2661	12	16.8667
61.8728	13	10.1870
66.8828	14	00.7764
71.1424	15	— 11.5271
74.5096	16	— 26.8033
76.8579	17	— 45.0410
78.0785	18	— 66.1313
78.0829	19	— 89.8650
76.8053	20	— 115.9231
74.2043	21	— 143.8937
70.2638	22	— 173.2606
64.9945	23	— 203.4174
58.4336	24	— 233.6765
50.6449	25	— 263.2810
41.7181	26	— 291.4193
31.7676	27	— 317.2426

$$\gamma = 8^\circ - 7'$$

$$v = 0.99$$

π_n	n	$\psi_n = v\pi_n - 1 - \overline{v^2\pi'_n}$
<hr/>		
1.0000	1	0.9900
2.9700	2	2.8806
5.8508	3	5.4967
9.5552	4	8.5840
13.9708	5	11.8243
18.9622	6	14.8397
24.3746	7	17.2185
30.0880	8	18.5288
35.7709	9	18.3390
41.3856	10	16.2380
46.6927	11	11.8565
51.5060	12	4.8860
55.6474	13	— 4.9026
58.9515	14	— 17.6423
61.2706	15	— 33.3566
62.4780	16	— 51.9490
62.4722	17	— 73.1963
61.1799	18	— 96.7459
58.5582	19	— 122.1179
54.5966	20	— 148.7105
49.3176	21	— 175.8114
42.7774	22	— 202.6125
35.0650	23	— 228.2387
26.8006	24	— 251.7207
16.6842	25	— 272.1209
6.2417	26	— 288.4611
— 4.6777	27	— 299.8028

$$\gamma = 9^\circ - 56'$$

$$v = 0.985$$

π_n	n	$\psi_n = v\pi_n - 1 - v^2\pi'_n$
<hr/>		
1.0000	1	0.9850
2.9550	2	2.8214
5.7767	3	5.2501
9.3368	4	7.9034
13.4717	5	10.3277
17.9891	6	12.0136
22.6748	7	12.4296
27.3010	8	11.0587
31.6352	9	7.4365
35.4493	10	1.1879
38.5281	11	— 7.9395
40.6784	12	— 20.0464
41.7367	13	— 35.0590
41.5761	14	— 52.7152
40.1123	15	— 72.5590
37.3074	16	— 93.9446
33.1730	17	— 116.0515
27.7709	18	— 137.9084
21.2125	19	— 158.4272
13.6557	20	— 176.4443
5.3012	21	— 190.7703
— 3.6140	22	— 200.2125
— 12.8235	23	— 203.7808
— 22.0404	24	— 200.4467
— 30.9663	25	— 189.4951
— 39.3017	26	— 170.4260
— 46.7559	27	— 143.0269

$\pi - \gamma = 0^\circ$				
$\pi_n A_n$ Real	$\psi_n P_n$ Real	n	$\pi_n A_n$ Imaginary	$\psi_n P_n$ Imaginary
0.722	0.628	1	— 0.547	— 0.340
0.968	1.200	2	— 0.459	— 0.902
2.117	1.155	3	— 1.523	— 0.435
1.130	2.095	4	— 0.301	— 1.429
2.349	0.716	5	— 1.319	— 0.095
0.209	2.432	6	— 0.007	— 1.094
1.688	— 0.797	7	— 0.401	— 0.086
— 1.061	0.280	8	— 0.135	— 0.009
— 2.176	— 1.411	9	— 0.528	— 0.214
— 2.602	— 4.669	10	— 0.690	— 2.849
— 5.728	— 3.678	11	— 5.252	— 1.330
— 6.244	— 5.410	12	— 5.976	— 9.380
— 5.790	— 5.266	13	— 10.219	— 10.970
— 1.511	— 6.199	14	— 11.427	— 11.132
1.634	6.144	15	— 15.326	— 12.512
6.593	7.105	16	— 13.208	— 12.411
8.537	7.073	17	— 6.833	— 13.970
0.976	— 3.357	18	— 0.051	— 0.631
— 6.905	— 8.636	19	— 2.903	— 5.221
— 9.731	— 8.468	20	— 7.029	— 4.175
10.209	— 10.459	21	— 14.117	— 13.234
1.529	0.645	22	— 0.104	— 0.018
— 0.025	— 0.304	23		— 0.004
— 0.351	— 0.265	24	— 0.005	— 0.029
0.243	— 0.437	25	— 0.002	— 0.007
0.020	0.032	26		
0.003	0.003	27		
R = — 3.197 T = — 29.851		R' = — 101.365 T' = — 102.810		
R + T = — 33.049		R' + T' = — 204.175		
(R + T) ² = 1092		(R' + T') ² = 41687		
I ₁ = 42779				

$$\pi - \gamma = 7^\circ - 15'$$

$\pi_n A_n$ Real	$\psi_n P_n$ Real	n	$\pi_n A_n$ Imaginary	$\psi_n P_n$ Imaginary
0.722	0.623	1	-0.547	-0.338
0.960	1.162	2	-0.455	-0.873
2.075	1.077	3	-1.493	-0.406
1.090	1.856	4	-0.294	-1.266
2.219	0.593	5	-1.247	-0.079
0.193	1.855	6	-0.006	-0.834
1.512	-0.548	7	-0.359	-0.059
-0.918	0.169	8	-0.117	-0.006
-1.814	-0.725	9	-0.440	-0.110
-2.078	-1.955	10	-0.551	-1.193
-4.359	-1.173	11	-3.997	-0.424
-4.504	-1.170	12	-4.311	-2.028
-3.937	-0.590	13	-6.948	-1.228
-0.962	-0.046	14	-9.190	-0.082
0.969	-0.587	15	-9.086	1.202
3.612	-1.400	16	-7.236	2.453
4.289	-2.082	17	-3.432	4.113
0.446	1.298	18	-0.023	0.244
-2.852	4.081	19	-1.193	2.469
-3.559	4.675	20	-2.571	2.470
3.279	6.515	21	-4.535	8.244
0.425	-0.442	22	-0.029	0.013
-0.006	0.224	23	-0.000	0.003
-0.068	0.206	24	-0.001	0.002
0.038	0.354	25		0.006
0.002	-0.026	26		
	-0.002	27		

$$R = -3.226 \quad T = 13.945$$

$$R + T = 10.719$$

$$(R + T)^2 = 115$$

$$R' = -58.061 \quad T' = 12.293$$

$$R' + T' = 45.768$$

$$(R' + T')^2 = 2095$$

$$I_1 = 2210$$

$$\pi - \gamma = 8^\circ - 7'$$

$\pi_n A_n$ Real	$\psi_n P_n$ Real	n	$\pi_n A_n$ Imaginary	$\psi_n P_n$ Imaginary
0.722	0.622	1	-0.547	-0.337
0.958	1.153	2	-0.454	-0.866
2.064	1.058	3	-1.485	-0.398
1.080	1.798	4	-0.291	-1.227
2.187	0.564	5	-1.229	-0.075
0.189	1.719	6	-0.006	-0.773
1.469	-0.490	7	-0.319	-0.053
-0.885	0.144	8	-0.112	-0.006
-1.730	-0.575	9	-0.420	-0.087
-1.958	-1.378	10	-0.591	-0.811
-4.052	-0.661	11	-3.716	-0.239
-4.123	-0.339	12	-3.946	-0.588
-3.541	0.284	13	-6.249	0.591
-0.818	1.042	14	-8.100	1.870
0.835	-1.700	15	-7.825	3.178
3.029	-2.714	16	-6.068	4.753
3.486	-3.384	17	-2.790	6.684
0.349	1.899	18	-0.018	0.357
-2.139	5.550	19	-0.895	3.356
-2.530	5.997	20	-1.827	3.169
2.180	7.960	21	-3.014	10.072
0.258	-0.516	22	-0.018	0.015
-0.003	0.252	23	-0.000	0.003
-0.031	0.222	24		0.002
0.012	0.366	25		0.006
	-0.026	26		
	-0.002	27		

$$\begin{aligned} R &= -3.022 \quad T = 18.845 \\ R + T &= 15.823 \\ (R + T)^2 &= 250 \end{aligned}$$

$$\begin{aligned} R' &= -49.950 \quad T' = 28.867 \\ R' &= -21.083 \\ (R' + T')^2 &= 444 \end{aligned}$$

$$I_1 = 694$$

$$\pi - \gamma = 9^\circ - 56'$$

$\pi_n A_n$ Real	$\psi_n P_n$ Real	n	$\pi_n A_n$ Imaginary	$\psi_n P_n$ Imaginary
0.722	0.619	1	-0.547	-0.335
0.953	1.129	2	-0.452	-0.848
2.038	1.010	3	-1.466	-0.381
1.055	1.656	4	-0.284	-1.129
2.109	0.493	5	-1.185	-0.065
0.179	1.391	6	-0.006	-0.626
1.367	-0.351	7	-0.325	-0.038
-0.801	0.086	8	-0.102	-0.003
-1.530	-0.233	9	-0.371	-0.035
-1.677	-0.101	10	-0.445	-0.062
-3.344	0.442	11	-3.066	0.160
-3.256	1.390	12	-3.117	2.411
-2.656	2.030	13	-4.687	4.226
-0.598	3.112	14	-5.713	5.589
0.516	-3.697	15	-5.123	7.566
1.809	-4.908	16	-3.623	8.596
1.851	-5.365	17	-1.482	10.597
0.159	2.707	18	-0.008	0.509
-0.775	7.201	19	-0.324	4.534
-0.633	7.115	20	-0.457	3.760
0.234	8.637	21	-0.324	10.929
-0.022	0.510	22	0.001	0.015
0.001	0.225	23		0.003
0.026	0.176	24		0.002
-0.023	0.225	25		0.004
-0.002	-0.015	26		
	-0.001	27		

$$R = -2.271 \quad T = 24.461$$

$$R + T = 22.190$$

$$(R + T)^2 = 492$$

$$R' = -33.106 \quad T' = 55.419$$

$$R' + T' = 22.313$$

$$(R' + T')^2 = 498$$

$$I_1 = 990$$

VISCOSITIES OF AQUEOUS SOLUTIONS

By

G. S. KASBEKAR

IN connection with some other work which is in progress in this laboratory, it was found necessary, owing to lack of data in literature, to determine the viscosities of solutions of zinc chloride, calcium thiocyanate, zinc thiocyanate and phosphoric acid. For the same reason too, densities of calcium and zinc thiocyanate solutions had to be measured. The results of these measurements are embodied in this paper.

EXPERIMENTAL

All reagents employed in this investigation were analytical reagents supplied by the British Drug Houses and were certified to be of high standard of purity. Solutions of various concentrations of the salts were prepared by weight dilution from saturated solutions carefully filtered through a sintered glass funnel. Syrupy phosphoric acid was used for preparing solutions of that acid. The strength of the solution was determined by the estimation of both the components of the salt and only those solutions were employed where the concentrations as determined by the estimation of both the ions agreed within 0.2 per cent. Zinc was estimated with potassium ferrocyanide using methyl red as an adsorption indicator (Tananaew and Georgofini. *Zeit. Anal. Chem.* 1936, 107, 92). Potassium palmitate method (Hamer. *J. Soc. Chem. Ind.* 1935. T. 205) was employed to estimate calcium. Chlorides were estimated with silver nitrate by the simplified potentiometric method (Callan and Horrobin. *J. Soc. Chem. Ind.* 1928, 47, 329-43) and the thiocyanates by the use of the same reagent but with ferric alum as an indicator. Wilkie's (*J. Soc. Chem. Ind.* 1909, 28, 68) method was adopted to estimate phosphoric acid.

Measurements of density were made by weighing a constant volume of the solution in a specific gravity bottle. The bottle

filled with the solution was left in a thermostat for at least two hours before the final weighing. Duplicates of density measurements were accepted only when the difference in weights was less than 0.008 per cent. Viscosity was measured with a simple type of Ostwald viscometer as modified by Jones and Veazey (Zeit. Physik. Chem. 1905, 61, 641) with a capillary diameter of less than 0.25 mm. and with a water-flow of 72.0 seconds. Duplicates in viscosity measurements were accepted only when the times of flow did not differ by more than 0.1 sec. All the above experiments were carried out in water thermostat regulated at $25 \pm 0.02^\circ\text{C}$.

RESULTS AND DISCUSSION

In tables I—IV are recorded the results of viscosity measurements of solutions of zinc chloride, calcium thiocyanate, zinc thiocyanate and phosphoric acid respectively. In connection with the viscosity measurements, densities of solutions of calcium thiocyanate and zinc thiocyanate had to be determined. Densities of these solutions are recorded in tables V and VI. The viscosity results are expressed as relative viscosity ($\eta_{\text{H}_2\text{O}}=1$).

TABLE I

Viscosities of solutions of zinc chloride at 25°C .

Conc. of solution		Relative viscosity η	A
per cent. by wt.	molality <i>m.</i>		
3.08(*)	0.233	1.108	1.551
6.14(*)	0.481	1.202	1.467
10.44	0.863	1.291	1.344
21.02	1.960	1.587	1.267
42.40	5.405	2.810	1.211
55.10	8.993	5.314	1.202
57.65	9.979	6.606	1.209
62.76	12.36	10.29	1.208
67.53	15.26	19.04	1.214
73.10	19.97	44.83	1.210
75.02	22.04	84.43	1.223

(*) Wagner (Zeit. Physik. Chem. 1891, 5, 31).

TABLE II

Viscosities of solutions of calcium thiocyanate at 25°C.

Conc. of solution		Relative viscosity η	A
per cent. by wt.	molality <i>m.</i>		
8.69	0.6092	1.16	1.276
19.52	1.552	1.494	1.295
31.30	2.919	2.360	1.342
40.48	4.355	3.880	1.366
51.13	6.699	10.97	1.430
57.45	8.644	29.79	1.481
57.98	8.835	32.00	1.481

TABLE III

Viscosities of solutions of zinc thiocyanate at 25°C.

Conc. of solution		Relative viscosity η	A
per cent. by wt.	molality <i>m.</i>		
8.778	0.5313	1.198	1.273
17.07	1.132	1.474	1.409
26.56	1.993	1.995	1.415
34.43	2.894	2.760	1.420
38.70	3.477	3.300	1.409
42.19	4.021	3.938	1.406

TABLE IV

Viscosities of solutions of phosphoric acid at 25°C.

Conc. of solution		Relative viscosity η	A
per cent. by wt.	molality <i>m.</i>		
8.54(*)	1.000	1.273	1.273
12.92	1.513	1.400	1.249
28.39	4.041	2.327	1.232
38.81	6.469	3.467	1.212
57.49	13.79	7.883	1.162
72.11	26.39	17.860	1.115
75.93	32.18	22.64	1.102
77.91	35.97	26.34	1.095
80.83	43.00	33.19	1.085
83.85	52.95	39.77	1.076
86.80	67.05	49.44	1.059
89.15	83.77	66.67	1.052

(*) Reyher (Zeit. Physik. Chem. 1886, 2, 744).

TABLE V

Densities of solutions of calcium thiocyanate at 25°C.

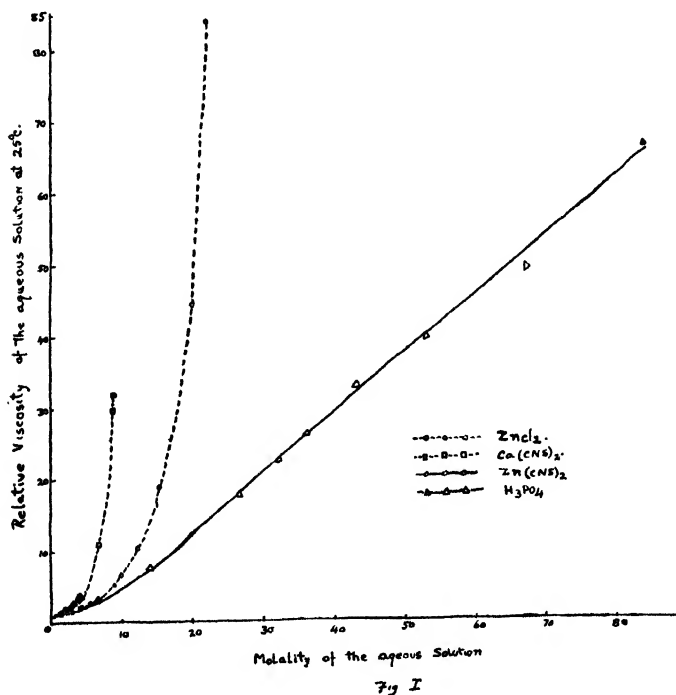
Concentration of solution		Density at 25°C. gm./c.c.
per cent. by weight	Molality	
8.69	0.6092	1.0511
19.52	1.552	1.1213
31.30	2.919	1.2002
40.48	4.355	1.2704
51.13	6.699	1.3516
57.45	8.644	1.4012
57.98	8.835	1.4053

TABLE VI

Densities of solutions of zinc thiocyanate at 25°C.

Concentration of solution		Density at 25°C gm./c.c.
per cent. by weight	Molality	
8.778	0.5304	1.0532
17.07	1.132	1.1103
26.56	1.193	1.1805
34.43	2.893	1.2489
38.70	3.477	1.2837
42.19	4.021	1.3143

It is found that with the exception of zinc thiocyanate, the other substances give highly viscous solutions when concentrated.

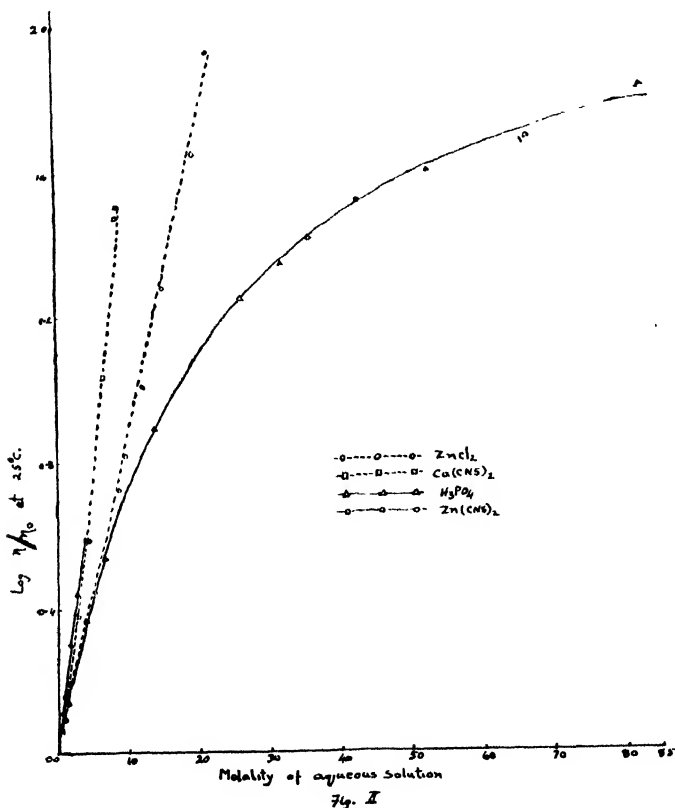


The viscosity concentration curves for salt solutions (fig. 1) are

exponential and fig. 2. shows that for them the relation between $\log \eta$ and m (molality of the solution) is represented by a straight line. This indicates that the relation between viscosity and concentration could be expressed by the empirical equation of Arrhenius (Zeit. Physik. Chem. 1887. 1. 285),

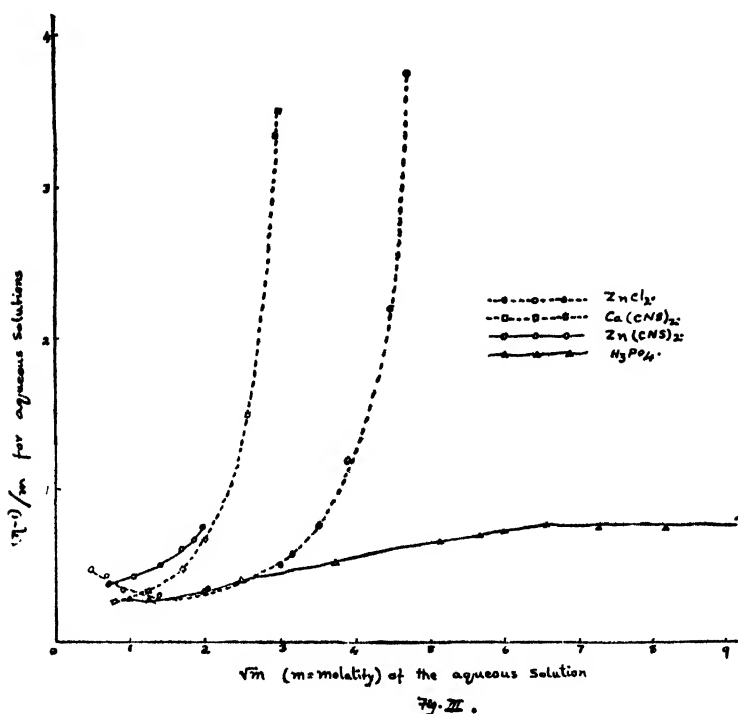
$$\eta = A^m, \text{ where } A \text{ is a constant.}$$

The value of the constant 'A', however, is found to be different in each case. The calculated values of A are also entered in



tables I-IV. The more dilute solutions do not conform to this relation but the agreement is satisfactory specially at the higher concentrations. The values of 'A' cannot be called exactly a constant with solutions of phosphoric acid. For dilute solutions 'A' seems to be almost a constant but departure from constancy becomes marked as concentrations increase beyond ten molar.

Grüneisen (Wiss. Abh. d. Phys. Tech. Reichsanst. 1905. 4. 239) had found for eighteen salts that the expression $(\eta-1)/m$



had a minimum. This was further confirmed by Appleby (Jour. Chem. Soc. 1910, 97, 2000), Merton (J. Chem. Soc. 1910, 97, 2454) and by Jones and Dole (J. Amer. Chem. Soc. 1929, 51, 2950). The results of these workers appear to show that $(\eta-1)/m$ decreases rapidly with increasing concentration in very dilute solution, passes through a minimum and then increases slowly. One can see from fig. 3 in which $(\eta-1)/m$ is plotted against \sqrt{m} (instead of m , for convenience of graphical presentation) that with zinc chloride and phosphoric acid the value does pass through a minimum. This could not, however, be confirmed with the other substances as no measurements were made at very low concentrations.

Grüneisen (loc. cit.) tried to explain the existence of the minimum in the viscosity increment—concentration curve in terms of the degree of dissociation of the solute and Applebey (loc. cit.) suggested the necessity of taking into consideration certain factors, like the number of single and triple water

molecules present in the solution. But it could be stated, in general, that since the viscosity of a solution is determined by the molar concentration of the salt, by the degree of ionisation and association of the solute and the solvent, and by the degree of hydration of the salt and its ions, it appears that the decrease in the rate of increase of viscosity with concentration is in all probability due to a decrease in the molecular species in the solution. Although the concentration of the solution is increasing, this apparent decrease in molecular species is brought about by the decrease in the ionisation of the salt with its increasing concentration. As the concentration of the solution increases beyond that corresponding to the minimum, association of the solute in all probability, plays an important part in causing a rapid increase in viscosity.

SUMMARY

Density and viscosity have been measured by the well established methods. It has been possible to show that the relation between viscosity and concentration is adequately represented by the empirical formula suggested by Arrhenius (loc. cit.) and that with zinc chloride and phosphoric acid the values of $(\eta-1)/m$ pass through a minimum as has been previously observed by Grüneisen (loc. cit.) and others, for other solutions.

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NEUTRAL TINT LIGHT FILTERS

By

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NEUTRAL tint or grey light filters are useful in optical experiments, much in the same way as the well known neutral wedge, by which light intensity from a suitable source could be controlled to any desired extent. While such filters are not easily procurable for the infra red and the ultra-violet regions, glasses as well as gelatin films having a more or less uniform cut off throughout the visible region are commercially available. In form of solution perhaps the only filter of qualitatively known composition is the one mentioned by Goldberg (Trans. Farad. Soc., 1923, 19, 349). A grey coloured solution is also made by E. Leitz but its composition is unknown. It was therefore considered desirable to attempt the preparation of such filters both in the form of solution as well as gelatin films. The present work is restricted to the visible part of the spectrum.

EXPERIMENTAL

Inorganic salts.—A neutral tint filter prepared from pure inorganic salts soluble in water, would be easily reproducible from a given set of data, and thus a standard grey filter would be available whenever required. Unfortunately, the few known inorganic coloured salts do not offer any wide choice in making up the required grey tint. It seems that at least one coloured organic ingredient has to be mixed in the combined filter or used in a separate cell. With this limitation the filter described below seems to be satisfactory.

At first pairs of aqueous solutions showing complementary colours were tried. The only pair which apparently gives a grey colour on mixing is a combination of nickel and cobalt salt solutions. The green solution of nickel salts has transmission in the green and absorption in the red and violet parts of the spectrum, while the red cobalt salt solution has its absorption in the green and transmission in the violet region. These two

salt solutions were mixed in varied proportions systematically, but it was found that under no circumstances they could give a uniform transmission from $\lambda 7000\text{\AA}$ to $\lambda 4000\text{\AA}$. The spectrophotometric curve for this mixture shows too high transmission in the orange and the violet regions. After a number of observations it was found that if aqueous solutions of potassium chromate for compensation in the violet, and of copper chloride for compensation in the red were added to the original nickel cobalt mixture, an almost neutral coloured solution was obtained. However a drawback still remained in that the transmissions for $\lambda 6000\text{\AA}$ to $\lambda 5500\text{\AA}$ were a little higher than the other wave lengths. To overcome this difficulty a blue organic colour soluble in water had to be used, as there is no suitable inorganic salt of this colour showing selective absorption in this region. Such a colour was found in the dye Soluble Blue (B. D. H.) which has an absorption band in the desired part. This dye may be mixed with the solution-mixture of the inorganic salts mentioned above, but the resulting mixture although giving a neutral tint does not show good keeping quality. It is therefore more advisable to use it in a separate cell.

The following table shows the composition and transmission of this filter :—

TABLE I

Nature of the composition	Composition of the filter	Density $\log I_0/I$	P. C. transmission	Fig. 1 curve
Inorganic salts and an organic dye.	17.0 c. c. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (10 gms. dissolved in 100 c. c. water), 45.0 c. c. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (10 gms. dissolved in 100 c. c. water), 0.6 c. c. K_2CrO_4 (1 g. dissolved in 100 c. c. water) and 1.5 c. c. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (10 gms. dissolved in 100 c. c. water). Th = 2 cms. for the mixture and 1 cm. cell of 0.002 gms. of Soluble Blue dissolved in 100 c. c. of water.	0.75	16	A

To get a higher percentage of transmission both the solutions can be diluted. The dilution law holds good and by diluting twice one can obtain 40 p. c. transmission throughout the visible spectrum.

Filters from Organic Dyes.—Unlike the coloured inorganic salts, for the preparation of a neutral tint filter from organic

dyes, we have a wide variety of choice for innumerable red, green and blue dyes. A large number of such dyes were examined for this purpose and finally one of the sets selected was made up from (1) Congo red (B. D. H.), (2) Naphthol Green (I. C. I.) and (3) Victoria Blue (B. D. H.).

In more ways than one these dyes are to be preferred to others. They are fairly fast to ordinary light from tungsten filament lamps and can be easily absorbed on gelatin without much bleeding. Thus they are useful either in solution or on gelatin film for making a neutral filter. Congo Red transmits the red region fully upto $\lambda 6300\text{\AA}$ and shows complete absorption beyond, while Naphthol Green has its absorption band in the red from $\lambda 7200\text{\AA}$ to $\lambda 6234\text{\AA}$. The transmission of Victoria Blue extends from $\lambda 4900\text{\AA}$ to $\lambda 4000\text{\AA}$. Now first of all the red dye and the green one are mixed till the resulting solution does not show colour of any of its components. The yellowish mixture thus formed is ultimately neutralized by Victoria Blue to get a grey tint. This neutral filter gives a fairly uniform transmission from the red end of the spectrum to the violet (Fig. 1, curve B).

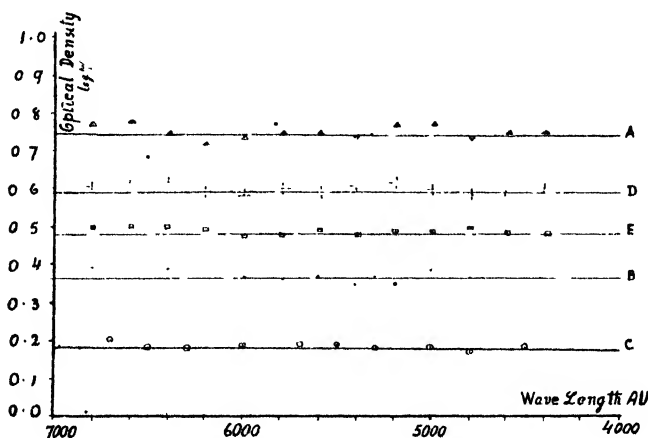


Fig. 1.

Black Dyes as Neutral Tint Filters.—Black dyes may be looked upon physically as made up of all the visible colours in right proportion and should provide in solutions good neutral tint filters. It is found, however, that almost all black dyes give a violet tinge in dilute aqueous solutions. After an examination of all the available dyes it was found that only one of them known as "Artificial Silk Black GN" (Ciba) was the

best, as it did not show any colour other than neutral grey even in dilute solutions. It is also possible to dye gelatin films with this dye at any suitable concentration and obtain a more convenient series of graded filters.

TABLE II

Nature of the composition	Composition of the filters	Density $\log I_0/I$	P. C. transmission	Fig. 1 curve
Mixture of organic dyes.	4.2 c.c. Victoria Blue (0.02 gms. dissolved in 100 c.c. water), 5.5 c.c. Congo Red (0.02 gms. dissolved in 100 c.c. of water), 30 c.c. Naphthol Green (0.02 gms. in 100 c.c. water). The mixture was diluted 4 times Th = 1 cm.	0.36	45.0	B
Black Dye.	Artificial Silk Black GN 0.001 gms. in 100 c.c. of water Th = 1 cm.	0.18	69.0	C

Neutral tint gelatin films.—Neutral tint gelatin filters were also prepared since these are more convenient in use than the liquid solution filters described before. Such filters are obtained either (1) by incorporating in gelatin dyes of primary colours and subsequently combining them, or (2) by dyeing gelatin films with black dyes. A third type of neutral gelatin filter may also be obtained by making use of a darkened photographic plate. In all these cases of gelatin dyeing, Ilford 'Ordinary' photographic plates ($2\frac{1}{2} \times 3\frac{1}{2}$ ") were used after proper fixing and washing in the dark. If desired these dyed gelatin films could be stripped off from the plate and mounted between better quality plane or optically finished glasses.

(1) COMBINATION OF FILTERS DYED WITH PRIMARY COLOURS

It has been mentioned before that by suitably combining the dyes Congo Red, Victoria Blue and Naphthol Green a neutral tint solution can be prepared. Now if gelatin films are dyed with these dyes individually, and afterwards combined to make one filter a neutral tint filter is obtained. For dyeing gelatin films it is necessary that the concentrations of the dye baths should be fairly high and each filter should be dyed in a number of shades or densities. By a suitable combination of these graded filters of three colours a neutral tint filter may be obtained.

Another combination used in the preparation of a composite neutral tint filter was (1) Eosine, (2) Orange II and (3) Brilliant Green. The concentrations of the dye baths were 0.2, 0.4, 0.6, 0.8 and 1.0 p.c. The dyed gelatin glass strips having been prepared were suitably combined to get a neutral filter. In the following table the combination of such gelatin dyed filters prepared from specified dye concentrations is shown. The mean density value of the filter is also given.

TABLE III

Dye filter combination		Conc. of the dye bath	Mean Density	P. C. transmission
Eosine	...	0.25 p. c.		
+	...			
Orange II	...	0.20 p. c.	1.2	6.0
+	...			
Brilliant Green	..	0.20 p. c.		

(2) GELATIN DYED WITH BLACK DYES

'Art Silk Black GN' which was the dye chosen for making one of the liquid grey filters was used to dye gelatin films on plates at definite concentrations for various amounts of time. A set of graded filters was thus obtained.

A 0.002 p.c. solution of this dye was made and photographic plates $3\frac{1}{2} \times 2\frac{1}{2}$ " after being fixed and washed were put in the dye bath. Four plates were thus dyed for 25, 35, 45 and 100 secs. After drying and mounting them in the usual manner their optical densities were determined on the spectrophotometer at various wave lengths. The average value of the density in each of the above cases was 0.18, 0.24, 0.32 and 0.59 respectively. In Fig. 1 the curve D shows the density of the filter (average value 0.59) which was bathed in the dye for 100 secs.

(3) DARKENED PHOTOGRAPHIC PLATES AS NEUTRAL TINT FILTERS

Since the work of Goldberg (loc. cit.) it is well known that the developed grains of silver on a photographic plate can act as neutral tint filters. In comparison with the other substances the dark silver grains are very stable and sufficiently neutral.

A photographic negative also serves the same purpose. By exposing low speed and fine grained plates to the graded illumination, or by varying the time of exposures or by controlling the development, a series of filters of different densities may be obtained which could be afterwards calibrated on the spectrophotometer. In any case the developing should be carried out with a fresh developer.

The result of one series of experiments carried out in this connection are shown in table IV. In all the cases mentioned the plates (Ilford "Ordinary") were exposed at a distance of 1 meter to a low voltage lamp (12 volts, 6 watts.) considerably underrun.

TABLE IV

Plate No.	Time of exposure in secs.	Time of developing in secs.	Density of the plate. $\log I_0/I$
1	1.0 secs.	40 secs.	0.10
2	1.0 secs.	60 secs.	0.12
3	1.5 „	20 „	0.15
4	1.5 „	40 „	0.18
5	1.5 „	60 „	0.20
6	1.5 „	120 „	0.32
7	1.5 „	180 „	0.39
8	3.0 „	120 „	0.48

The spectrophotometric curve for one of the neutral tint filters (No. 8) thus prepared is shown in Fig. I, curve E.

SUMMARY

A number of neutral grey filters in form of (1) Inorganic salt solutions mixture, (2) Organic dye solutions mixture, (3) Dyed gelatin and (4) Photographic negative have been prepared and their optical densities are determined on a spectrophotometer.

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MUTUAL COAGULATION OF COLLOIDAL SOLUTIONS

PART IV—INTERACTION OF ZINC FERROCYANIDE AND (a) FERRIC HYDROXIDE, (b) THORIUM HYDROXIDE AND (c) CERIC HYDROXIDE

By

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IN previous papers^{1, 2, 3} published from our laboratory it has been shown that in the case of mutual coagulation of -vely charged prussian blue and copper ferrocyanide by +vely charged ferric hydroxide, thorium hydroxide and ceric hydroxide sols, the width of the zone of mutual coagulation is minimum when the charge on the colloidal particles of the reacting sols is maximum, and that the fact whether the peptising electrolytes and other impurities present in the sols chemically react or not on mixing them does not affect the relation between the width of the zone of mutual coagulation and the charge on the colloidal particles. In the present paper similar results obtained with -vely charged zinc ferrocyanide and +vely charged ferric hydroxide, thorium hydroxide and ceric hydroxide are presented. The stabilising electrolytes $K_4Fe(CN)_6$ and HCl chemically react on mixing as in the case of copper ferrocyanide and ferric hydroxide, thorium hydroxide and ceric hydroxide sols³.

EXPERIMENTAL

Zinc ferrocyanide was precipitated by adding a solution of potassium ferrocyanide to a solution of zinc sulphate. The

precipitate was filtered and washed three to four times with distilled water to remove soluble impurities. It was then suspended in distilled water in a flask and 0.1% $K_4Fe(CN)_6$ solution was added to it in small amounts and the mixture shaken vigorously till a clear colloidal solution of zinc ferrocyanide was obtained. The colloidal solution was filtered four times through a double fold of filter papers in order to obtain, as far as possible, uniformity of particle size.

Ferric hydroxide, thorium hydroxide and ceric hydroxide sols were prepared in the same manner as done by Desai and co-workers^{1, 2}.

Dialysis of the sols and measurements of the charge on the particles, *i.e.*, determination of the cataphoretic speed were carried out as before^{1, 2, 3}.

The zone of coagulation was first determined roughly by finding out in each case the amounts of the two reacting sols at which turbidity first appears and then disappears, the total volume of the mixtures being kept 10 c.c. The zone of complete coagulation was afterwards accurately determined by taking a number of mixtures in the boundary region of the zone previously roughly determined by varying the amount of the colloids by 0.05 c.c. The mixtures were then centrifuged for 3 minutes at about 2500 r. p. m. and examined for complete coagulation. When the presence of a small amount of colloid was not readily determined in the supernatant liquid by visual observation, the latter was pipetted off and treated with an excess of suitable electrolyte solutions. The absence of any turbidity on standing was taken as an indication that no colloid was present in the supernatant liquid.

RESULTS AND DISCUSSION

The results of charge measurements are given in Table I and of mutual coagulation in Tables II, III and IV.

TABLE I

Days of Dialysis	Cataphoretic speed $\times 10^5$			
	Zinc ferro-cyanide	Ferric hydroxide	Thorium hydroxide	Ceric hydroxide
0	17.2	26.3	28.9	14.3
3	34.0
4	18.7	36.1	18.1
7	25.2
8	23.6	47.6	38.1
11	32.4	63.4	33.6
12	41.3
15	41.1	42.9
16	78.8	42.6
19	34.7
20	30.3	41.9	32.4
23	29.3
24	27.5	23.6
25	21.8

TABLE II

Mutual coagulation of zinc ferrocyanide by ferric hydroxide.
 (Numbers in different columns refer to c.c. of ferric hydroxide in 10 c.c. of the mixture of zinc ferrocyanide and ferric hydroxide.)

A = Appearance of turbidity. Z = Zone of coagulation.
 D = Disappearance of turbidity).

		Days of dialysis of zinc ferrocyanide																				
		0			4			8			11			15			20			25		
		A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D	A	Z	D
Days of dialysis of ferric hydroxide	0	0.2	<u>5.8</u>	6.0	0.2	5.8	6.0	1.1	5.3	6.4	2.5	4.0	6.5	0.9	2.9	3.8	0.8	1.1	1.9	1.0	0.3	1.3
	4	0.7	6.3	7.0	0.3	<u>4.5</u>	4.8	0.9	3.3	4.2	1.9	1.5	3.4	2.0	0.3	2.3	0.6	0.6	1.2	0.5	0.5	1.0
	8	2.1	7.8	9.9	1.4	4.9	6.3	1.0	<u>4.1</u>	5.1	0.3	3.7	4.0	1.0	1.3	2.3	0.3	1.7	2.0	1.0	0.7	1.7
	11	1.0	8.1	19.1	1.1	5.1	6.2	0.5	4.6	5.1	0.6	<u>3.1</u>	3.7	0.2	0.2	0.4	0.4	1.7	2.1	0.9	0.5	1.4
	16	1.7	7.5	9.2	1.0	6.2	7.2	0.9	4.9	5.8	0.2	0.6	0.8	1.3	<u>0.1</u>	1.4	0.4	2.4	2.8	2.0	0.5	2.5
	20	1.0	8.3	9.3	1.2	6.5	7.7	0.9	6.6	7.5	0.7	5.1	5.8	0.4	4.3	4.7	0.4	<u>3.9</u>	4.3	0.5	4.6	5.1
	23	2.8	6.3	9.1	1.6	6.4	8.0	0.7	6.7	7.4	0.3	6.4	6.7	0.5	5.3	5.8	0.5	4.5	5.0	0.3	<u>4.0</u>	4.3

TABLE III

Mutual coagulation of zinc ferrocyanide by thorium hydroxide.

(Numbers in different columns refer to c. c. of thorium hydroxide in 10 c. c. of the mixture of zinc ferrocyanide and thorium hydroxide.

A = Appearance of turbidity. Z = Zone of coagulation.
D = Disappearance of turbidity).

		Days of dialysis of zinc ferrocyanide											
		0			4			8			11		
Days of dialysis of thorium hydroxide		A	Z	D	A	Z	D	A	Z	D	A	Z	D
		A	Z	D	A	Z	D	A	Z	D	A	Z	D
0		1.6	<u>4.4</u>	6.0	1.9	3.8	5.7	1.7	3.3	5.0	1.3	3.1	4.4
3		1.4	4.7	6.1	1.7	<u>4.3</u>	6.0	1.6	3.9	5.5	1.2	2.3	4.5
8		1.5	4.8	6.3	1.4	4.1	5.5	1.8	<u>4.0</u>	5.8	1.0	3.6	4.6
12		1.1	5.4	6.5	1.6	4.3	5.9	1.9	4.4	6.3	0.8	<u>4.0</u>	4.8
16		1.3	5.5	6.8	1.3	4.9	6.2	1.5	4.6	6.1	1.3	4.3	5.6
20		1.2	6.1	7.3	1.3	5.4	6.7	1.4	4.9	6.3	1.1	4.7	5.8
24		1.1	6.6	7.7	1.2	5.8	7.0	1.3	5.3	6.6	1.1	5.1	6.2

TABLE IV

Mutual coagulation of zinc ferrocyanide by ceric hydroxide.

(Numbers in different columns refer to c. c. of ceric hydroxide in 10 c. c. of the mixture of zinc ferrocyanide and ceric hydroxide.

A = Appearance of turbidity. Z = Zone of coagulation.
D = Disappearance of turbidity).

		Days of dialysis of zinc ferrocyanide											
		0			4			8			11		
Days of dialysis of ceric hydroxide		A	Z	D	A	Z	D	A	Z	D	A	Z	D
		A	Z	D	A	Z	D	A	Z	D	A	Z	D
0		0.8	<u>8.0</u>	8.8	1.2	7.1	8.3	1.1	6.6	7.7	0.8	6.1	6.9
4		0.9	8.2	9.1	1.0	<u>6.6</u>	7.6	1.3	6.0	7.3	1.4	5.4	6.8
7		0.7	8.4	9.1	1.3	5.8	7.1	0.7	<u>6.5</u>	7.2	1.2	6.5	7.7
11		1.1	8.5	9.6	1.1	6.2	7.3	1.2	5.4	6.6	1.0	<u>6.4</u>	7.4
15		1.0	8.6	9.8	1.0	6.5	7.5	1.0	5.8	6.8	0.9	6.3	7.2
19		0.9	8.8	9.7	1.2	6.8	7.0	1.3	6.1	7.4	1.1	6.6	7.7
24		0.7	9.1	9.8	1.1	7.1	8.2	1.1	6.5	7.6	1.0	6.5	7.5

It will appear from Table I that with the progress of dialysis the charge on the colloidal particles or the cataphoretic speed first increases, reaches a maximum and then decreases for all the sols. The initial increase in cataphoretic speed is due to some of the oppositely charged ions which are bound with the primarily adsorbed, *i.e.*, preferentially adsorbed similarly charged ions as a result of electrical adsorption, becoming free as their concentration in the sol diminishes during dialysis; the final decrease in cataphoretic speed is due to desorption of the preferentially adsorbed similarly charged ions from the surface of the particles, *i.e.*, from the inner sheet of the double layer as their concentration in the intermicellary liquid becomes very low in the latter stages of dialysis^{1, 4}.

From Tables II, III and IV it will be seen that the variation in the value of 'Z' when to one sol dialysed for a certain period another sol dialysed for different periods is added is not quite regular. This is due to the fact that sols dialysed for different periods have different amounts of impurities in them and they will affect the charge on the colloidal particles differently. When, however, one considers the value of 'Z' underlined in the Tables, *i.e.*, when both the sols dialysed for nearly the same period are allowed to interact, it is found that the zone of mutual coagulation first decreases, reaches a minimum and then increases with the progress of dialysis. On comparing the periods in Tables II, III and IV when the value of 'Z' is minimum with those given in Table I when the charge is maximum for the same sols during dialysis, it will appear that the minimum value of 'Z' and maximum value of charge occur at about the same period, *i.e.*, 14 to 16 days. These results are thus in line with those obtained in earlier papers^{1, 2, 3}.

According to Weiser and Chapman⁵ the factors which one has to consider as being important in the process of mutual coagulation are (1) electric neutralisation of charge, (2) mutual adsorption of the colloidal particles, (3) interaction between stabilising ions, and (4) the presence of free electrolytes in the sol. It will appear that the factor (3) in this case as well as for mutual coagulation of -vely charged copper ferrocyanide by +vely charged hydroxide sols⁸ has been operative. Its influence will decrease with dialysis as the concentration of the stabilising ions in the intermicellary liquid decreases. The value of 'Z' has, however, first decreased and then increased. This factor is therefore not important. Factor (4) is also similarly not important in all the cases. The influence of factor (2) will

be to neutralise charge and hence will be maximum when the charge on the particles of both the sols is highest. The mutual adsorption of the particles of one sol by those of the other should therefore first increase and then decrease.

Let us now consider the effect of the first factor mentioned above, *i.e.*, of electric neutralisation of charge. If the charge on the particles of one of the sols which is in excess is highest, the amount of the oppositely charged colloid required to be added to coagulate it, will have to be sufficiently large so as to lower down the charge to such a value that aggregation can take place, producing turbidity; similarly the disappearance of turbidity or its appearance from the other end (*i.e.*, when the second colloid is in excess and its particles have the highest charge) will occur when large amount of coagulating colloid from that end is added. Thus the zone of precipitation will be narrowest, *i.e.*, the value of 'Z' will be smallest when the particles of both the sols have greatest charge. It is also clear that when the charge on the particles is small, *i.e.*, for the undialysed or long period dialysed sols, the value of 'Z'—the zone of mutual coagulation—will be largest.

From the foregoing discussion it will appear that our results do not support generalisation of Weiser and Chapman (*loc. cit.*) that the zone of mutual coagulation is quite narrow if both the sols contain little or no free electrolyte, although their other generalisation that the zone is widest for impure sols is supported by all our experiments tried so far.

It will also be seen that the lowest value of 'Z' for all the pairs tried is in the order 0.1, 1.7 and 6.2 units for zinc ferrocyanide and ferric hydroxide, zinc ferrocyanide and thorium hydroxide and zinc ferrocyanide and ceric hydroxide, respectively. This is in line with our previous results^{2, 3}. This is probably due to the fact that of the three +vely charged hydroxide sols, the particles of ceric hydroxide are most hydrated while those of ferric hydroxide are relatively least hydrated. In what way however, hydration actually affects the lowest value of 'Z' is not quite clear.

SUMMARY AND CONCLUSIONS

Mutual coagulation of the pairs zinc ferrocyanide and ferric hydroxide, zinc ferrocyanide and thorium hydroxide and zinc ferrocyanide and ceric hydroxide has been studied with the progress of dialysis. It is observed that the width

of the zone of mutual coagulation is minimum when the charge on the particles is maximum, the width first decreasing and then increasing and the charge first increasing and then decreasing with the progress of dialysis. The minimum value of the width of the zone of mutual coagulation in different pairs also seems to depend upon the hydration of the colloidal particles of the +vely charged hydroxide sols.

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KINETICS OF REACTIONS IN HETEROGENEOUS SYSTEMS

PART VI—HYDROLYSIS OF ACID HALIDES BY WATER

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IN continuation of previous work by Karve and collaborators (Karve and Dole, Jour. Ind. Chem. Soc., 1935, 12, 719-739; Jour. Uni. Bom. 1938, 7, Part III, 108-126. Karve and Mehendale, Jour. Uni. Bom., 1939, 8, Part III, 160-170) a detailed study of the hydrolysis of phthalyl, benzoyl and m-nitrobenzoyl chlorides has been carried out, with a view to explain the mechanism of heterogeneous reactions in liquid-liquid systems.

In the previous investigations (Loc. cit.) the liquid-liquid heterogeneous systems were roughly classified as (i) homo-heterogeneous and (ii) purely heterogeneous ones. The reaction between aromatic acid halides dissolved in monochlorobenzene and water is a reaction of the second type. The study of the homo-heterogeneous reactions is complicated by the mutual solubility of the reactants in the two phases and therefore no universally applicable formula has yet been found for such reactions. The purely heterogeneous reactions are comparatively easy for study and may be considered to be analogous to the reactions in the solid-liquid heterogeneous systems, in which the reactions take place at the surface of contact of the two phases and the velocity of the reactions is determined by the speed of diffusion of the reactants and of the reaction products to and from the surface of contact. It was expected, and later on

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observed, that some of the characteristics of solid-liquid heterogeneous systems were common to the purely heterogeneous reactions in liquid-liquid systems.

Three important views have so far been put forward to explain the heterogeneous reactions in solid-liquid systems. According to the modified Noyes-Whitney-Nernst theory of 'diffusion layer' (*Zeit. physikal. chem.* 1897, 23, 689-692 ; 1904, 47, 52), a saturated layer of reaction products is formed at the surface of contact and the velocity of reaction depends upon the diffusion of the reaction products from this layer into the surrounding medium. The velocity of reaction will depend upon the slower of the two processes. If the chemical reaction is slower, then it will govern the velocity of the reaction, and if the 'diffusion' process is slower, it will in turn determine the velocity of the reaction.

The diffusion layer theory has been severely criticized by Ericson-Auren (*Zeit. anorg. chem.* 1898, 18, 83 ; 1901, 27, 209), Wildermann (*Zeit. physikal. chem.* 1909, 66, 445), Roller (*J. Phys. Chem.* 1931, 35, 1133 ; 1932, 36, 1202 ; 1935, 39, 221), and by Palmaer (*Zeit. physikal. chem.* 1906, 56, 689). Wildermann claims that the assumption of a diffusion layer is unnecessary, since the same velocity equations can be derived without its use. He, further, showed that the diffusion layer theory could not explain the dependance of the velocity of solution of gypsum on the physical properties of the material and variation with different faces of the crystals. In order to explain these facts the 'Adsorption layer' theory has been advocated. That the Noyes-Whitney-Nernst theory of heterogeneous reaction velocity is not adequate for all solid-liquid reaction systems is supported by the studies in velocities of crystallization in solution by Marc (*Zeit. physik. chem.* 1908, 61, 385 ; 1909, 67, 470 ; 1909, 68, 104 ; 1910, 73, 685). He indicates that since the rate of crystallization is inhibited by the presence of foreign substances, this must be due to the adsorption layer formed at the surface of the growing crystal. The existence of such a layer is also indicated by an initial rapid fall in supersaturation during the first half minute after the crystals have been added to the supersaturated solution. The most important systems, in which the adsorption phenomenon is predominant, are the catalytic processes in solid-liquid interfaces. The reactants in this case are adsorbed on the face of the catalyst forming a layer on the surface of the catalyst. The adsorption layer theory cannot be applied to liquid-liquid systems directly, since in the case of catalysts both the reactants

are adsorbed on the surface of the finely divided solid. The adsorption phenomenon influences the liquid-liquid heterogeneous systems in a somewhat different manner and it is discussed in detail in the present investigation.

In the opinion of Roller (*loc. cit.*) there is no necessity for the assumption of either a diffusion layer or an adsorption layer. The measured rate of fluid-phase heterogeneous reaction is considered to be simply the resultant of two simultaneous processes of chemical reaction at the interface and physical transport to or from the interface—with no arbitrary assumption as to the mechanism of the reaction. The reactions can be explained on the basis of known physical and chemical laws. But it seems that this view is also not universally applicable, since in some cases definite proof of adsorption phenomena has been obtained, *e.g.*, in the case of contact catalysis.

Recently King (*J. Am. Chem. Soc.*, 1935, 57, 828-831) has attempted to answer the criticism on Nernst's theory by slightly modifying the conceptions of the 'diffusion layer'. According to him there is no sharply defined adhering layer and the thickness of the layer varies with the speed of stirring and diffusion coefficient of the reagents.

The adsorption layer theory has been advocated by Bell (*J. Phys. Chem.*, 1928, 32, 882-893) for liquid-liquid heterogeneous systems. In these systems both the phases being mobile, attractive forces of the molecules play their own part. The influence is perceptible at the surface of contact, where the reaction takes place.

When two immiscible liquids come in contact with each other, molecules of solute (if any) in the liquids are adsorbed either positively or negatively at the surface of the two liquids in contact with each other. The chemical reaction will take place by the collision of molecules on the adsorbed molecules at the surfaces.

Bell (*loc. cit.*) has studied the reaction between benzoyl-*o*-toluidide dissolved in benzene and aqueous potassium permanganate solution. Since electrolytes in general are adsorbed negatively, he assumes that a positively adsorbed film of benzoyl-*o*-toluidide is formed at the surface of contact in the benzene phase and the permanganate ions strike on this film producing reaction. But his experimental results were not confirmed by Kassel and Schaffer (*J. Amer. Chem. Soc.*, 1929, 51, 965) who repeated the work next year. Some of these experiments were also repeated by us with our apparatus but

our mode of shaking had a tendency to form an emulsion of the two phases and the results are not strictly comparable. He (*i.e.*, Bell) observed that (1) the velocity of reaction is independent of the intensity of agitation, (2) the velocity is directly proportional to the concentration of potassium permanganate, (3) the temperature coefficient is 13, and (4) the Gibbs-Helmoltz eqn. for adsorption could be verified in this system. Bell's observations have been contradicted by Kassel and Schaffer (*loc. cit.*). Bell's assumption that the influence of manganese dioxide formed during the first stages of reaction may be negligible, is not correct. I agree with Kassel and Schaffer, that the colloidal manganese dioxide is not so stable and a third solid phase is introduced in the reaction. The most important observation of Kassel and Schaffer, with whom I agree, is, that the reaction is dependent on stirring, that is the intensity of agitation. The above authors have not given due consideration to this point since it was not their main object of study. Their main object of investigation was the temperature coefficient of the reaction, which, according to Bell was 13, and according to Kassel and Schaffer 2; and the latter observation seems to be correct. They also observed that the temperature coefficient increases with temperature. Although the temperature coefficient of the same reaction was not studied in the present investigation, it was studied in detail in other reactions. The results agree with those of Kassel and Schaffer and the explanation of the increase in the temperature coefficient with temperature is that, there is a small amount of homogeneous oxidation of benzoyl-o-toluidide due to its slight solubility in water and also the solubility of benzene in the aqueous phase. With the rise of temperature the solubility of benzoyl-o-toluidide in the aqueous phase increases, thus causing an increase in the homogeneous part of the reaction, and therefore the increase in the temperature coefficient of the reaction.

According to Kassel and Schaffer, the main thesis of the work of Bell (that a saturated monomolecular adsorbed layer is formed at the surface of a concentrated solution of the non-electrolyte and the reaction results by the permanganate ions striking this layer) is not affected by their work. But the reaction must be considered as a special case wherein special precautions were taken to avoid strong solutions of electrolytes which always disturb the adsorption phenomenon. Verification of the Gibbs-Helmoltz equation supports the formation of an 'adsorbed layer' but this verification was made only by assuming that the permanganate solutions were very dilute and that the

interfacial tension was the same as that of pure water. This assumption has no validity.

Lastly, the fact that the reaction is dependent on stirring the two layers independently without disturbing the surface of contact cannot be explained by the 'adsorption layer' theory. It is obvious that since the reaction is dependent on stirring and since Kassel and Schaffer had taken every precaution to keep the surface of contact undisturbed, it seems that diffusion of reaction products is influenced by speed of stirring. The conclusion is, that a monomolecular adsorbed layer may form on the surface of the non-electrolyte but that is not the only factor which affects the velocity of reaction. Diffusion of reagents and of reaction products to and from the surface of contact also affect the velocity of reaction to a considerable extent.

In the present investigation I have attempted to prove that in liquid-liquid heterogeneous systems there are two important factors besides other factors of mutual solubility, etc., which govern the rate of reaction: (1) The adsorption of one of the reagents on the surface of one of the solvents, and (2) the diffusion of reaction products and the reagents to and from the surface of contact. The second factor has been proved to be in existence in the solid-liquid heterogeneous systems.

The picture of the reaction system as studied by Karve and collaborators in previous investigations of this series (*loc. cit.*) was as follows:—The agitation of the reaction flasks splits up the phases into droplets. Each droplet behaves as a separate entity and the reaction takes place at the surface of each droplet. A layer of the reaction products is formed round each droplet and the velocity of the chemical process is governed by the rate of the diffusion of the products, etc. from this layer into the surrounding medium. If the diffusion process is slower than the chemical process, then the reaction velocity is governed by the diffusion process. If the chemical process is slower of the two, it governs the reaction velocity.

In the present investigation it has been found that adsorption of the molecules of the acid chloride may take place at the surface of the non-aqueous layer under certain conditions and influences the rate of reaction.

EXPERIMENTAL

The experimental arrangements were the same as in the previous investigations (Karve and Dole, *Jour. Uni. Bom.*, 1938, 7, Part III, 108-126). In it reaction velocities of 15 acid halides

were studied with change of concentrations, addition of neutral electrolytes, etc. It was found during these investigations that individual values of K in each experiment gradually increased with time, and this was attributed partly to the mode of shaking and partly to an unknown cause. Although one of the expected causes was the catalytic influence of the inorganic acid produced during the reaction, it was found that the influence of the inorganic acid was retardation of the reaction due to its electrolytic influence, rather than of a catalytic nature. Recently it has been observed that a part of the increase in K is due to the catalytic action of the organic acid produced. The influence was confirmed by addition of a known amount of soluble organic acid to the reaction system.

1. INFLUENCE OF ADDITION OF ORGANIC ACID TO THE REACTION SYSTEM

Con. of phthalyl chloride in	
monochlorobenzene	... 0.05 M
∞ reading in c.c.s N/10 AgNO ₃	... 18.5 c.c.
aqueous phase (with the organic acid)	50.0 c.c.
Non-aqueous phase	... 10.0 c.c.
Temperature	... 30.0°C.

TABLE I
Addition of phthalic acid in various concentrations.

Time in Min.	K with pure water	K with 0.02 N acid	K with 0.04 N acid	K with 0.06 N acid	K with 0.08 N acid
15	0.00387	0.00439	0.00467	0.00520	0.00531
30	0.00396	0.00462	0.00477	0.00522	0.00545
45	0.00412	0.00476	0.00506	0.00538	0.00565
60	0.00427	0.00486	0.00514	0.00550	0.00571
75	0.00440	0.00488	0.00523	0.00527*	0.00496*
90	0.00453	0.00512	0.00527	0.00497*	0.00462*
Mean	0.00419	0.00475	0.00499	0.00536	0.00560

* Solid phthalic acid separated due to its insolubility in these concentrations.

(The mean calculated is from readings at 30, 45 and 60 minutes only, so as to make the comparison more relevant. Since separation of solid phthalic acid causes a retardation of the reaction, the other readings cannot be taken for calculating the mean. Similarly, the first reading is always low and therefore left out of the calculations).

TABLE II

Time in Min.	K with pure water	K with 0.1 N C H ₃ COOH	K with 0.03 N C ₆ H ₅ COOH	K with 0.03 N m-C ₆ H ₄ NO ₂ COOH
15	0.00387	0.00475	0.00475	0.00598
30	0.00396	0.00508	0.00539	0.00637
45	0.00412	0.00505	0.00547	0.00664
60	0.00427	0.00506	0.00559	0.00668
75	0.00440	0.00507	0.00555	0.00676
90	0.00453	0.00508	0.00564	0.00692
Mean	0.00419	0.00506	0.00553	0.00668

These tables indicate clearly the influence of the addition of an organic acid on the velocity of hydrolysis. The increase in the value of K is nearly proportional to the ionisation of the acids. But strict proportionality will not be found due to the influence of various other effects produced by the addition of acids to the system, *e.g.*, change in the interfacial tension, specific gravity of the aqueous phase, etc.

There is one very curious fact to note that the addition of m-nitrobenzoic acid to the reaction system water and m-nitrobenzoyl chloride has no influence on the values of K. They remain constant. But the hydrolysis of phthalyl chloride is accelerated by its addition.

2. INFLUENCE OF CONCENTRATION OF NEUTRAL ELECTROLYTES ON THE HYDROLYSIS OF ACID CHLORIDES

In the previous investigations the influence of electrolytes was found to be one of retardation of the reaction. In order to find the relation between the concentration and the retardation of reaction, hydrolysis of 0.5 phthalyl chloride was studied by addition of sodium sulphate in varying quantities to the aqueous phase.

All the other factors were kept the same as in 1 above. The temperature was 30.0°C.

TABLE III

Time in Min.	Water pure	0.1 M Na_2SO_4	0.2 M Na_2SO_4	0.4 M Na_2SO_4	0.6 M Na_2SO_4	0.8 M Na_2SO_4	1.0 M Na_2SO_4
15	0.00387	0.00380	0.00277	0.00201	0.00160	0.00103	0.00103
30	0.00396	0.00355	0.00311	0.00218	0.00173	0.00122	0.00097
45	0.00412	0.00357	0.00315	0.00220	0.00180	0.00123	0.00101
60	0.00427	0.00361	0.00320	0.00232	0.00181	0.00125	0.00102
75	0.00440	0.00371	0.00325	0.00234	0.00184	0.00127	0.00104
90	0.00453	0.00381	0.00332	0.00238	0.00186	0.00127	0.00105
Mean	0.00419	0.00365	0.00321	0.00228	0.00181	0.00125	0.00102

It will be easily seen, that the retardation varies with the concentration of the sodium sulphate added.

Similarly, the following table will show that the hydrolysis of m-nitrobenzoyl chloride is influenced by the addition of the neutral electrolyte.

TABLE IV

Time in Min.	30	60	90	120	150	180	Mean
K with pure water	0.00237	0.00238	0.00239	0.00240	0.00240	0.00240	0.00239
K with 0.1 M Na_2SO_4	0.00202	0.00211	0.00215	0.00216	0.00217	0.00217	0.00213

0.5 M m-nitrobenzoyl chloride solution was used. Temp. 30.0°C .

3. A STUDY OF THE HYDROLYSIS OF O-IODOBENZOYL CHLORIDE

In our previous investigation (Karve and Dole, Jour. Uni. Bom., 1938, 7, 108) iodobenzoyl chloride gave rather abnormal value of K. Instead of a regular increase in the values of K, there was obtained a regular decrease. This decrease appeared to be no matter of chance, but in both the concentrations studied, the same fact was observed. Therefore it was thought necessary to study the reaction more carefully and in greater detail. It was found that the reaction is quite normal with fresh solutions of iodobenzoyl chloride but the solutions which had been kept for some time gave results similar to our previous experiments (loc. cit.). It was the usual practice in all these and previous investigations to employ only freshly prepared solutions of the acid halides. It was only by an accident that in

the case of iodobenzoyl chloride this practice was changed. Attention was drawn towards the phenomenon by some abnormal values of K in the hydrolysis of 0.5 M phthalyl chloride by 1.0 N Na_2SO_4 solution. In one of the experiments, where probably a one day old solution of the acid chloride was used, I obtained regularly decreasing values of K . But when the experiment was repeated with a fresh solution of phthalyl chloride, normal results were obtained. In order to collect more data on this point the hydrolysis of 0.5 M phthalyl chloride was studied by pure water with (1) a fresh solution of phthalyl chloride, (2) a one day old solution of phthalyl chloride, and (3) a five day old solution of phthalyl chloride. These experiments indicated no great abnormality in the results, except that the values of K in general increased with the age of the solutions. (It must be pointed out here that the phthalyl chloride solutions were kept in good glass stoppered bottles and the stoppers were smeared with a little vaseline so as to prevent any contact with air). The increase in the value of K in the last two experiments could be explained by the fact that a very small quantity of the acid chloride is hydrolysed by the moisture present in the air in the bottle, and the organic acid produced must be reacting catalytically. It was also observed that when the solutions of acid chlorides were stored in bottles filled to the neck and stoppers sealed with paraffin wax, no rise was shown in the values of K , after storing for four days.

The summary of all these observations is given in the following table :—

TABLE V

Temp. 30.0°C.	o-Iodobenzoyl chloride : results of previous investigation		Fresh solution of iodobenzoyl chloride
Time in Min.	0.25 M acid chloride	0.5 M acid chloride	0.5 M acid chloride
15	0.00176	0.00198	0.00176
30	0.00162	0.00188	0.00196
45	0.00160	0.00186	0.00205
60	0.00157	0.00183	0.00207
75	0.00153	0.00180	0.00198*
90	0.00151	0.00179*	0.00170*
Mean	0.00157	0.00183	0.00202

Mean of the readings after 30, 45 and 60 minutes is calculated.

* Solid iodobenzoic acid separated.

TABLE VI

Hydrolysis of phthalyl chloride; 0.5 M solution. Temp. 25.0°C.

Time in Min.	Fresh solution	One day old solution	Five days old solution
15	0.00270	0.00277	0.00295
30	0.00292	0.00297	0.00341
45	0.00302	0.00309	0.00350
60	0.00311	0.00320	0.00351
75	0.00315	0.00325	0.00355
90	0.00322	0.00327	0.00358
Mean	0.00308	0.00316	0.00351

Mean of the last five readings is calculated.

TABLE VII

Hydrolysis of 0.5 M phthalyl chloride by 1.0 M Na_2SO_4 .

Time in Min.	15	30	45	60	75	90	Mean
Fresh acid chloride sol.	0.00103	0.00097	0.00101	0.00102	0.00104	0.00105	0.00102
One day old acid chloride solution	0.00111	0.00109	0.00107	0.00106	0.00104	0.00103	0.00107

The explanation for the decrease of individual values of K observed in case of old solutions is given in the following way:—

As the acid chloride grows old, some of it is slightly hydrolysed by the moisture of the air and the corresponding organic acid which is liberated during the hydrolysis remains dissolved in the monochlorobenzene phase. In the case of the hydrolysis of phthalyl chloride by pure water, this organic acid (*i.e.*, phthalic acid) is partitioned between the two phases (due to its appreciable solubility in water) and the part in the aqueous phase catalyses the reaction, and the values of K increase regularly.

In the other two cases, however, the phenomenon is quite different. First of all in the hydrolysis of iodobenzoyl chloride, the solubility of iodobenzoic acid in water at ordinary temperature is very small (0.0952 gms. per litre at 25.0°C). Thus when the acid chloride is hydrolysed, the aqueous phase is rapidly

saturated by iodobenzoic acid and the rest of the iodobenzoic acid then begins to dissolve in the monochlorobenzene phase, in which it is also soluble to a certain extent. In the monochlorobenzene phase, the acid chloride is positively adsorbed at the surface of the phase. When iodobenzoic acid begins to go into solution in the monochlorobenzene it is also positively adsorbed at the surface of the non-aqueous phase. But in doing so it displaces the previously adsorbed acid chloride at the surface, since there is a limit of adsorption at the surface, depending on the surface forces acting at the surface of contact. Thus the concentration of the acid chloride at the surface of contact of the two phases is diminished and hence the decrease in the reaction. Similarly, I have observed that whenever solid acid is separated, even though in small quantities—the rate of reaction as seen by the value of K rapidly slows down.

Now in the case of hydrolysis of phthalyl chloride by 1.0 M aqueous sodium sulphate, the same phenomenon is observed. The solubility of phthalic acid produced during the reaction is greatly diminished by the presence of the concentrated solution of sodium sulphate. So, as soon as the aqueous phase is saturated with phthalic acid, the acid begins to dissolve and get adsorbed at the surface of the monochlorobenzene phase. And in doing so it displaces the previously adsorbed phthalyl chloride from the surface, thus diminishing the reaction.

In both cases when fresh solutions are used no decrease in values of K is observed, since there is no previously liberated acid due to slight hydrolysis of the acid chloride. However, in case of iodobenzoyl chloride there is a decrease in later stages of the reaction (which in a way supports the above explanation).

The above explanation also satisfactorily accounts for the maximum value of the first K with old solutions of the acid chlorides (see Table VII). The acid liberated catalyses the reaction in the beginning when its influence is counteracted by the adsorption phenomenon in the later stages of the reaction, and the values of K gradually decrease.

In the light of this explanation the retardation of reaction by the addition of electrolytes can be explained in the following way :—

The introduction of an electrolyte causes a diminution in the solubility of the acid liberated during the reaction in the phase. The organic acid therefore dissolves to a greater extent in the monochlorobenzene phase, where it is adsorbed positively at the surface of the phase, displacing the previously adsorbed acid

chloride, thus causing a diminution of the concentration of the acid chloride at the surface of contact, where the reaction is taking place.

Another proof for the fact that the organic acid is displaced from the aqueous phase into the monochlorobenzene phase is obtained by observing the catalytic activity of the organic acid after the addition of an electrolyte. If the organic acid is displaced from the aqueous phase the catalytic activity of the acid will also diminish. A kind of rough measurement of the diminution of the catalytic activity of the organic acid can be obtained by calculating the difference in the values of K between the 2nd and 6th readings in an experiment. (The first value of K is always discarded since, in nearly all cases, it is too low). By referring to table No. III, the following difference can be noted:—

TABLE VIII

Con. of Na_2SO_4	Diff. numerical	Con. of Na_2SO_4	Diff. numerical
Pure water	0.00057		
0.1 M	0.00026	0.6 M	0.00013
0.2 M	0.00021	0.8 M	0.00005
0.4 M	0.00020	1.0 M	0.00007

It can be concluded that the catalytic activity of phthalic acid diminishes proportionately to the increase in the concentration of sodium sulphate. The influence can be clearly appreciated, if it is remembered that the catalytic activity of organic acids (*i.e.*, weak acids) is accelerated by the addition of neutral salts of strong acids. Arrhenius (*Zeit. phys. chem.*, 1899, *31*, 197), found that the rate of inversion of sucrose by weak acids was greatly augmented by the addition of neutral salts of strong acids. For example, the presence of 0.125 N potassium chloride increases the catalytic activity of 0.025 N acetic acid by 12 per cent.

4. A STUDY OF THE TEMPERATURE COEFFICIENTS

In the previous investigation temperature coefficients of three reactions were studied between 26°–36°C. The hydrolysis of (1) benzoyl chloride, (2) phthalyl chloride, and (3) *m*-nitrobenzoyl chloride. Since temperature coefficients are important clues in the elucidation of the mechanism of heterogeneous reactions, they were again studied very carefully in the present investigation. The above-mentioned reactions were repeated at the temperatures 25° and 35°C. It has been found that the previous values have to be corrected to a certain extent, the trend of the coefficients remaining unaffected.

It was pointed out in the previous investigation that low temperature coefficients (about 1.0 to 1.5 per ten degrees rise) of reactions indicate a predominance of diffusion factors in the system and the normal temperature coefficients (about 2.5 per ten degrees rise) indicate the predominance of chemical factors in the system (Brunner and Tolloczko. *Zeit. phys. chem.*, 1900, 35, 283).

The carefully measured temperature coefficients are as follows :—

TABLE IX

Concentration of benzoyl chloride	1.0 M
„ phthalyl „	0.5 M
„ o-iodobenzoyl „	0.5 M
„ m-nitrobenzoyl „	0.5 M

Temp. 25°C.

Time in Min.	Benzoyl chloride	Phthalyl chloride	o-iodobenzoyl chloride	Time in Min.	m-nitrobenzoyl chloride
15	0.0103	0.00270	0.00117	30	0.00147
30	0.0118	0.00292	0.00136	60	0.00153
45	0.0118	0.00302	0.00137	90	0.00154
60	0.0123	0.00311	0.00139	120	0.00153
75	0.0123	0.00315	0.00141	150	0.00153
90	0.0122	0.00322	0.00142	180	0.00154
Mean	0.0121	0.00308	0.00139	mean	0.00153

Temperature 35°C.

15	0.0163	0.00531	0.00233	30	0.00361
30	0.0195	0.00598	0.00272	60	0.00386
45	0.0197	0.00612	0.00278	90	0.00389
60	0.0194	0.00620	0.00285	120	0.00389
75	0.0202	0.00633	0.00293*	150	0.00389
90	0.0195	0.00636	0.00269*	180	0.00392
Mean	0.0196	0.00619	0.00282	Mean	0.00389

K 35° 0.0196
K 25° 0.0121 = 1.62; $\frac{0.00619}{0.00308} = 2.00$; $\frac{0.00282}{0.00139} = 2.02$; K 35° 0.00389
K 25° 0.00153 = 2.54.

* Solid o-iodobenzoic acid separated at this stage.

The previous values for the temperature coefficients between 26° and 36° were 1.57, 1.85 and 2.54 for benzoyl chloride, phthalyl chloride, and m-nitrobenzoyl chloride, respectively. This indicates that in the hydrolysis of benzoyl, phthalyl, and o-iodobenzoyl chlorides, diffusion factors mainly determine the reaction velocity, while in the case of m-nitrobenzoyl chloride, the chemical process governs it.

The influence of neutral electrolytes on the temperature coefficients was expected to be very interesting. Firstly, it was expected that it would retard the diffusion process and in that case the temperature coefficient would be decreased. Secondly, by changing the surface properties of the phase it would affect the surface of contact. Thirdly, it would decrease the solubility of the reaction products (*i.e.*, the organic acid) and thus influence the adsorption phenomenon in the non-aqueous phase. In this case the temperature coefficients would increase.

In order to study the influence of neutral electrolytes on the temperature coefficients of the heterogeneous reactions, three acid chlorides were hydrolysed by 1.0 M solution of sodium sulphate.

All the other factors were the same as in the experiment indicated in table No. IX.

TABLE X

Time in Min.	Benzoyl chloride 25°	Benzoyl chloride 35°	Phthalyl chloride 25°	Phthalyl chloride 35°	Time in Min.	m-nitro-benzoyl chloride 25°	m-nitro-benzoyl chloride 35°
15	0.00201	0.00470	0.00060	0.00128	30	0.00053	0.00134
30	0.00248	0.00558	0.00060	0.00152	60	0.00057	0.00143
45	0.00258	0.00575	0.00064	0.00156	90	0.00059	0.00146
60	0.00274	0.00592	0.00065	0.00162	120	0.00059	0.00150
75	0.00288	0.00607	0.00067	0.00167	150	0.00058	0.00150
90	0.00292	0.00590	0.00069	0.00172	180	0.00059	0.00150
Mean	0.00272	0.00584	0.00065	0.00162	Mean	0.00058	0.00148
$\frac{K \text{ } 35^\circ}{K \text{ } 25^\circ}$	$\frac{0.00584}{0.00272} = 2.14$		$\frac{0.00162}{0.00065} = 2.49$			$\frac{0.00148}{0.00058} = 2.55$	

It will be observed here that there is practically no increase in the temperature coefficient of m-nitrobenzoyl chloride, while there is a distinct increase in the values of the temperature coefficients of benzoyl and phthalyl chlorides. In the first place

this indicates that the diffusion process of the system is not substantially influenced by the addition of a neutral electrolyte, since there is no lowering in the values of the temperature coefficients. There may be slight decrease in the velocity of diffusion of the reactants and the reaction products, but the influence on the chemical process seems to be more predominant. Secondly, the influence may be due to a change in surface properties of the phases, which amounts to change in the interfacial tension of the phases. The change in interfacial conditions is such that the adsorption of acid chloride molecules at the surface of monochlorobenzene is decreased, thus causing a diminution in the concentration of the acid chloride at the surface of contact. This means that there is a lowering in the reaction velocity, *i.e.*, in the chemical process. As the slower of the two processes is responsible for the speed of reaction, as soon as the speed of chemical process is less than that of the diffusion process, it begins to govern the rate of reaction. Consequently, the temperature coefficients tend to assume the value that is nearer the temperature coefficient of ordinary chemical reactions, *i.e.*, 2.5. The reaction in which the chemical process is already slower than the diffusion process there is no increase in the temperature coefficient, as it has already reached its normal value, *i.e.*, 2.5.

In the previous investigation, the temperature coefficients of the three reactions were measured between 26° to 36° C, at an interval of two degrees. The energy of activation of the reaction was calculated from these values of K and it was observed that the values of E (the energy of activation) were regularly increasing, indicating that the reaction is composite. The same phenomenon was observed by Kassel and Schaffer (*loc. cit.*) who repeated the experiments of Bell (*loc. cit.*).

The results of my measurements are given in the following Table :—

TABLE XI
Values of m-nitrobenzoyl chloride are given.

Temperature °C	Mean values of K	Energy of Activation
26	0.00165	24790
28	0.00198	25015
30	0.00239	25610
32	0.00287	26035
34	0.00349	26155
36	0.00420	

The curve of $\log K$ against $1/t$ is practically a straight line.

That the reaction is a composite one was also proved by the study of other factors. No further conclusions can be drawn from the values of E or the nature of the curve of $\log K$ against $1/t$.

5. DISCUSSION AND THE SUMMARY OF THE RESULTS

The following is a summary of the salient features of the investigation described before :—

- (1) Mineral acids retard the velocity of reaction of the reactions studied in the present investigation.
- (2) Organic acids accelerate the velocity of reaction to certain extent.
- (3) The addition of neutral electrolytes also retards the velocity.
- (4) The catalytic activity of organic acids is reduced by the addition of neutral electrolytes, since their concentration in the aqueous phase is lowered.
- (5) The study of the temperature coefficients and the calculations of the energy of activation indicate that the reactions are composite.
- (6) The temperature coefficients of the reactions increase on the addition of neutral electrolytes, except in the case of *m*-nitrobenzoyl chloride.

The above observations have been discussed at length in the preceding part. The mechanism of heterogeneous reactions has been mainly explained on the basis of either the "diffusion layer" or the "adsorption layer", by various authors. Bell (*loc. cit.*) has advocated the latter interpretation for liquid-liquid systems. My investigations, however, tend to indicate that both the influences are at work in liquid-liquid heterogeneous systems. And that there is no necessity of assuming a formation of layer, either diffusion or adsorption. The temperature coefficient of benzoyl chloride hydrolysis indicates that the diffusion factor predominates in the reaction, while the other data (the influence of neutral electrolytes on the velocity constant and the temperature coefficients) reveals that the adsorption factor is also responsible for the observed rate of reaction. It is equally important in the mechanism of

heterogeneous systems. The contention of Bell (*loc. cit.*) that the diffusion process does not influence the mechanism, since the reaction is independent of speed of stirring, is not supported by Kassel and Schaffer. The present investigation supports the work of Kassel and Schaffer. The reactions are dependent on stirring.

In short the conclusion that is arrived at is that both the diffusion factor and adsorption factor influence the course of the reaction. The mechanism of the reaction in liquid-liquid heterogeneous systems (studied according to the methods of Karve and Dole) can now be summarized in the following way:—Heterogeneous reactions in liquid-liquid systems are roughly classified into two groups—(1) The homo-heterogeneous, in which the homogeneous part is appreciable or predominant, and (2) the purely heterogeneous, in which the homogeneous part is negligible or absent. The majority of heterogeneous systems of liquid-liquid type belong to the first group, wherein mutual solubility of the reactants and reaction products influence the reactions. Kinetics of such reactions extend beyond the interface into the two phases. The net result in such cases may be due to a multiplicity of individual reactions each with their own characteristic and independent kinetic peculiarities. In purely heterogeneous systems the reactions take place at the surface of contact, and therefore, they are influenced both by the diffusion factor and adsorption phenomena. Concentrations of reactants at the surface of contact will depend upon the positive or negative adsorptions of the reactants at the surfaces of the two phases. While the diffusion of the reaction products away from the surface of contact into the interior of the phase will also influence the reaction. The diffusion process only reveals its influence when it is slower than the chemical process. The adsorption phenomenon, which may probably determine the velocity of the chemical reaction though existing all the while, is only clearly discernible when the chemical process is slower than the diffusion process.

Further work is in progress on the influence of stirring the two layers independently so that the surface of contact is kept constant. This is expected to throw more light on the nature and the influence of diffusion process. Also the relation between the surface properties of the individual phases and velocity of reaction is being studied by measuring the interfacial tensions between the phases.

SUMMARY

(1) The influence of mineral and organic acids on the hydrolysis of acid chlorides in liquid-liquid heterogeneous systems has been studied.

(2) The influence of concentrated solutions of neutral electrolytes indicates that both mineral acids and neutral electrolytes disturb the adsorption phenomenon of the system.

(3) The hydrolysis of o-iodobenzoyl chloride is studied and it is found that the reaction is normal and similar to the hydrolysis of other acid chlorides.

(4) The temperature coefficients of three reactions have been studied very carefully with and without addition of neutral electrolyte between the temperature 25° and 35°C.

It is found that the addition of neutral electrolytes raises the temperature coefficient and explanation is given for this observation.

(5) It has been found that both the diffusion factor and the adsorption phenomenon are responsible for the velocity of reactions in purely liquid-liquid heterogeneous reactions.

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[Received July 25, 1940]

PHOTOCHEMICAL DECOMPOSITION OF MALONIC ACID: $\text{HOOC} \cdot \text{CH}_2 \cdot \text{COOH}$

By

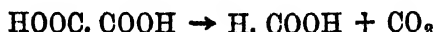
I. D. SHIVA RAO

ALREADY in 1896 Fay [Am. Chem. Journal, 18, 269, 1896] had noted a decomposition, though extremely slow, of malonic acid under the influence of direct sun rays, in the presence of a catalyser. According to Berthelot and Gaudechon, [Compt. Rend. 157, 333, 1923] uranium salts serve best the purpose. Volmar [*ibid.* 180, 1172, 1925] found out that the principal products of the photodecomposition of malonic acid are acetic acid and carbon dioxide:—



Pierce, Leviton and Noyce [J.A.C.S., 51, 80, 1929] also came to the same conclusion. According to them, malonic acid absorbs light in the ultraviolet region, and gets decomposed into acetic acid and carbon dioxide. The quantum efficiency is 0.75 ± 0.25 for 0.5 molar solution. They further asserted that the decomposition was due to the undissociated molecules, as the addition of strong acids did not alter the sensitivity of light.

Kailan [Monatsh, 34, 1209, 1913] and later A. J. Almond and L. Reeve [Jour. of Chem. Soc., 129, 2834, 1926] admitted that during the irradiation of malonic acid with a quartz mercury vapour lamp more COOH groups get decomposed than in the case of simple oxalic acid:—



Only here, a probable complex decomposition was suggested, and hence a complex of resulting acids and other organic compounds. The rest seem to have taken for granted that the

only products of decomposition were acetic acid and carbon dioxide. No definite qualitative or quantitative determinations were made to look for other substances. In a recent publication, however, A. Miolati and G. Semerano [Contributi alla Conoscenza di Alcuni Acidi Organici, Padova, 1937—a monogram], after their study of the formation of certain *labile* free molecules in electrolytic decompositions in the interphase $\text{Hg}/\text{H}_2\text{O}$, suggested the probable presence of other compounds as well, in the products of the photodecomposition of malonic acid. These would be the stable products of polymerisation of such free *labile* molecules, as CH_2 :, CH_2 . COOH , etc., which would be formed in the first instance, during the photo decomposition.

The following research was undertaken primarily, to study the various products of the photodecomposition of malonic acid, and thus secondarily, to derive some information as regards the nature of bonds between the carbon atoms in the molecules of this organic acid.

EXPERIMENTAL PART

The accompanying diagram shows the apparatus used. The solution of the acid was prepared in the flask A. Part of this solution remained there itself during the experiment. The quartz flask B, filled completely with part of the solution from A, was the vessel to contain the solution to be irradiated, and it was mounted mouth downwards under the quartz lamp. Ultra-violet rays were obtained from a Gallais and C^o, NL type, quartz lamp of 110 volts and 2.5 Amps. C_1 and C_2 were two capillary tubes through the rubber stopper closing the quartz flask. One end of C_1 was just inside the flask and the other end dipped in the solution in A. The end of C_2 inside B, was drawn to a point and was kept almost touching the bottom of the flask. The outer end of C_2 was bent and connected to the burette into which the gaseous products of the decomposition could be transferred, thus facilitating the transference of these products into the

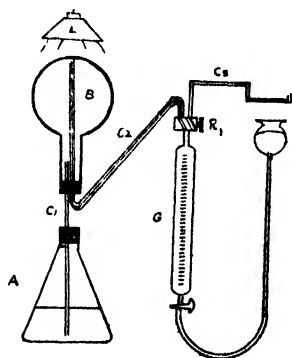


Fig. 1

The other end of the burette was connected to a mercury reservoir D, by means of pressure tubing filled with mercury.

EXPERIMENT I

7.590 gr. of malonic acid—Kahlbaum—were dissolved in 150 cc. of distilled water, previously boiled and cooled to expel all the air dissolved in it. Keeping the solution in the flask A and by adjusting the position of the mercury globe, the whole of the flask B and the two capillary tubes were completely filled with the solution. The capillary C₃ leading from the burette to the gas analysing apparatus was filled with mercury. The quartz lamp was mounted, well-centred and about 30 cms. above the flask, and the rays were concentrated by means of a conical metallic shade.

The irradiation, at various intervals, lasted 19 hours. After an hour's irradiation small bubbles of gas were noted. On account of the shade, the quartz flask was getting considerably heated so that the gas expanded and contracted on the lamp being lit and put out. Consequently the solution itself was getting agitated, being pushed out of and sucked into the flask B.

After 19 hours of irradiation, by repeated adjustments of the mercury globe, all the gas evolved was transferred into the Bone-Newitt gas analysing apparatus. The 33 cc. of gas on analysis at 14.5°C gave the following result :—

CO ₂	→	82	per	cent.
C ₂ H ₄	→	1.9	"	"
O ₂	→	0.9	"	"
CO	→	1.4	"	"
H ₂	→	2.1	"	"
[N ₂	→	11.6	"	"]

Ethylene was absorbed by mercuric nitrate in a saturated nitric solution of sodium nitrate, [Treadwell and Tauber, *Helv. Chim. Acta*, 2, 606], as according to G. Orlow, [B, 42, 894] bromine in bromine water does not absorb ethylene, when the latter is in a comparatively small quantity.

The following qualitative analysis of the irradiated solution was also done :—

(a) *Succinic acid*.—2 cc. of the solution were dried on a water bath, and the crystals obtained were mixed with an equal amount of disublimed resorcine in a clean dry test tube. It was then covered with 0.1 cc. of strong H₂SO₄ and was heated for five minutes at 120°C in an oil bath. After cooling

it was diluted with 50 cc. of distilled water and was rendered alkaline by means of ammonia. A yellowish green fluorescence indicated the presence of succinic acid. This was confirmed by repeating the test made simultaneously with the resorcline alone, a very light fluorescence was obtained. That done with the non-irradiated solution also gave only the light green fluorescence given by the resorcline alone. The fluorescence from the irradiated solution was characteristically bottle green and appeared sea green when seen across an ultraviolet lamp.

(b) *Oxalic acid*.—2 cc. of the irradiated solution was treated with H_2SO_4 and magnesium powder. When all the hydrogen was evolved the solution was filtered and dried on a water bath. The crystals obtained were gathered in a clean dry test tube and were heated in a water bath with 2 cc. of a solution of 2-7 dioxynaphthalein [0.01 gr. in 100 cc. of H_2SO_4]. The intense violet colour obtained would have proved the presence of oxalic acid, if the blank experiment with the sample of malonic acid had not given the same colouration. Oxalic acid was, therefore, tested for by the following method.

10 cc. of the irradiated solution was rendered alkaline with ammonia. To the alkaline solution an excess of a saturated solution of CaSO_4 was added. A heavy white precipitate was at once formed, which itself was indicative of the presence of oxalic acid. The precipitate was centrifuged and washed several times [to get rid of the malonic acid] with water, and was then treated as above with 2-7 dioxynaphthalein after reduction with magnesium powder and H_2SO_4 . An intense green colouration confirmed the presence of oxalic acid. The non-irradiated solution treated in the same way did not give a precipitate in the first stage.

(c) *Acetic acid*.—One cc. of the irradiated solution was neutralised with NaOH [Pnenolphthalein indicator]. To the neutral solution one more cc. of the irradiated solution was added, thus obtaining a semineutral solution. To this was added uranile formate obtained from uranile nitrate through ammonium uranate.

A few drops of this solution were placed on a crystallising plate, side by side with a blank experiment plate. When dry, on microscopic examination the presence of the characteristic crystals of the double acetate of sodium from the irradiated solution indicated the presence of acetic acid...

(d) *Fumaric acid*.—The polarographic analysis of the irradiated solution showed no perceptible quantity of fumaric acid.

EXPERIMENT II

With a view to the quantitative estimation of the products of decomposition during the irradiation, the experiment was repeated a second time. This time the apparatus was slightly modified as follows:—

(a) In order to avoid the heating of the vessel B, the metal shade of the quartz lamp was eliminated ;

(b) The quartz bulb B was fitted with only one capillary tube leading to the burette, so that the malonic acid was not agitated by the repeated "flow out" and "suck in" from the vessel on being heated and cooled ;

(c) The solution to be irradiated, was prepared in the quartz flask itself, dissolving 4.7304 gr. of malonic acid [Kahlbaum] in 108.8 cc. of distilled water previously boiled and cooled to get rid of the dissolved air. [The volume of the flask itself was 108.8 cc.].

The irradiation lasted 73 hours. The evolution of gas was very slow, the first bubbles becoming visible only after 48 hours of irradiation. This is certainly to be explained by the fact that during practically the whole of the irradiation the solution remained at the room temperature. Again the amount of CO is considerably higher. This is probably due to the fact that at low temperature and at slow evolution of the gas, the CO does not get oxidised to the more stable CO₂. Very likely, in the preliminary experiment part of the CO formed gets transformed to CO₂.

The analysis of the evolved gas gave the following results:—

The volume of the gas evolved	...	7.33 cc.
Temperature of analysis	...	18°C
CO ₂ [excluding that dissolved in sol.]	78.4	per cent.
C ₂ H ₄	...	1.8 per cent.
O ₂	...	1.0 per cent.
CO	...	10.9 per cent.
[N ₂	...	7.9 per cent.].

QUANTITATIVE DETERMINATIONS

(a) *Carbon dioxide dissolved in the solution.*—A current of air free from carbon dioxide was made to bubble through the original solution of malonic acid and the carbon dioxide dissolved in the solution was made to get displaced and then to be absorbed in barite water 0.0968 n., which was afterwards titrated against 0.0897 n. HCl [Phenolphthalein indicator]. On calculation it was found out that in the 108.8 cc. of the solution 37.1 cc. of carbon dioxide was dissolved. Remembering that only 7.33 cc. of the gaseous products were evolved, the percentages of the gaseous products were modified as follows :—

CO ₂	97.9 per cent.	CO.....	1.0 per cent.
C ₂ H ₄	0.2 per cent.	[N ₂	0.8 per cent.].
O ₂	0.1 per cent.		

From these the mole per cent. of these gaseous products were calculated :—

CO ₂	4.18 per cent.	CO.....	0.073 per cent.
C ₂ H ₄	0.012 per cent.	[N ₂	0.053 per cent.].
O ₂	0.007 per cent.		

(b) *Oxalic acid.*—10 cc. of the irradiated solution was neutralised with ammonia and to the neutral solution an excess of a saturated solution of calcium sulphate was added. The test tube in which a precipitate was being formed slowly, was set aside for three days. The solution was then filtered and the residue was repeatedly washed with a little water each time, first by decantation and then by washing on the filter. By the usual method of quantitative analysis the precipitate was dried, transferred to a weighed crucible, together with the filter paper and by strong heat was transformed into calcium oxide and weighed as such. From this weight 0.0012 gr., the quantity of malonic acid transformed into oxalic acid was calculated : 0.05 mole per cent.

(c) *Formic acid.*—The quantitative estimation of formic acid was done according to the method suggested by Von H. Ost and F. Klein [Ch. Z. 32, 816, IV] and modified by Rigamonti [Ann. di Chim. Applic. 22, 744, 1932].

10 cc. of the irradiated solution was neutralised by sodium hydroxide, and to the neutral solution [which contained also sodium acetate, from the simultaneously neutralised acetic acid], 2 cc. of mercuric chloride was added. The test tube was then

heated in a water bath for 2 hours. The same experiment was done on 10 cc. of the non-irradiated solution. The small amounts of precipitates obtained were dried at 105°C in small filter papers and weighed in a weighing cylinder.

From the two weights the quantity of formic acid in moles per cent. formed during the photodecomposition of malonic acid was calculated:—

$$\begin{aligned}\text{Weight of HgCl from 10 cc. of the irradiated solution} \\ = 1.9 \times 10^{-3} \text{ gm.}\end{aligned}$$

$$\begin{aligned}\text{Weight of HgCl from 10 cc. of the non-irr. solution} \\ = 3.51 \times 10^{-4} \text{ gm.}\end{aligned}$$

$$\begin{aligned}\text{HgCl due to the irradiation of 10 cc. of the acid} \\ = 1.55 \times 10^{-3} \text{ gm.}\end{aligned}$$

Remembering that the precipitation of HgCl comes about according to the following equation:—



that is to say, that for every molecule of formic acid correspond two molecules of mercurous chloride, the formic acid formed during the photodecomposition results as 0.008 moles per cent, moles of malonic acid.

(d) *Succinic acid*.—Through a fluorescence analysis only an approximate quantitative determination of succinic acid was done.

The following were separately evaporated to dryness on a water bath:—

- (a) 2 cc. of the irradiated malonic acid;
- (b) 2 cc. of the non-irradiated malonic acid;
- (c) 2 cc. of the non-irradiated malonic acid with 1 cc. of a succinic acid solution [0.010 gr. of the acid in 100 cc. of water].

In each of four clean dry test tubes exactly 0.1 gr. of disublimated pure resorcine was weighed. In each one of the three of these test tubes, the residue from each one respectively of the above was taken. To all the four test tubes 0.1 cc. of strong H_2SO_4 was added. The test tubes were heated at 120°C for five minutes in an oil bath. They were then well cooled and the contents dissolved in 5 cc. of distilled water, and the solutions rendered alkaline by 2 cc. of ammonia. A first comparison of the fluorescence was made in these strong solutions. A further

comparative study was made on dilution, and the following table gives the result at a glance :—

Dilution	2 cc. of orig. mal. ac. 0.1 gm. of resorcin 0.1 cc. of con. H_2SO_4	2 cc. of orig. mal. ac. 1 cc. of succ. acid 0.1 gr. of resorcin 0.1 cc. of con. H_2SO_4	2 cc. of irr. mal. ac. 0.1 gr. of resorcin 0.1 cc. of con. H_2SO_4	0.1 gr. res. 0.1 c.c. H_2SO_4
Residue	Yellow-Orange	Intense-Orange	Green	Light red
5 cc. H_2O 2 cc. NH_4OH	Strong green	Green	Strong green	Light green
Diluted five times	Fluorescence = a	Fluorescence = 2a	Fluorescence = 4a

A Comparative study of the above scheme gave 0.3 as the mole per cent. of succinic acid formed during the irradiation of malonic acid.

Further the absence, at least in sufficient quantity for qualitative analysis, of methyl alcohol was inferred [Compt. Rend. Soc. Biol. 199, 795, 1932].

1 cc. of the irradiated solution was slowly added with continuous agitation to 5 cc. of a Beckman solution [5 gr. of $K_2Cr_2O_7 + 30$ cc. of $H_2O + 2.8$ cc. of conc. H_2SO_4]. After five minutes the solution was microfiltered and 2 to 3 cc. of the distillate which ought to have contained the aldehyde if methyl alcohol was present, was collected. To the distillate an excess of dimedone [a solution of 0.5 parts of 3-5 dimethyl-dihydro-resorcinol in 100 parts of water] was added and the test tube containing this mixture was immersed in boiling water for about 10 minutes. The complete absence of even a trace of precipitate, and the immediate formation of one even when a small drop of methyl alcohol is present, showed the absence of methyl alcohol in the irradiated solution.

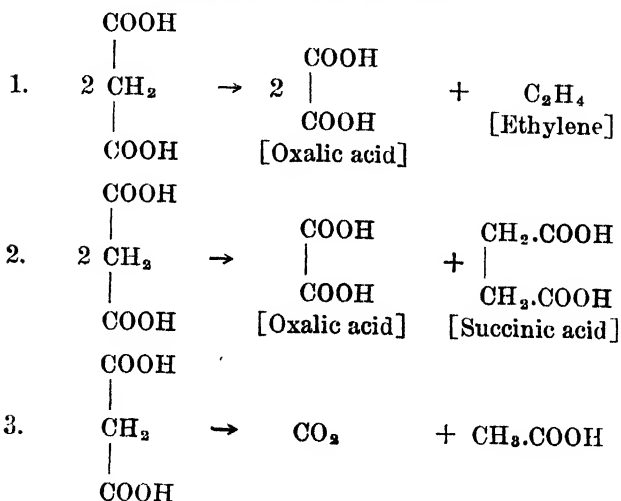
Glycolic acid was tested for qualitatively [Resenius and Bruckner, Z. Ann. Chem. 89, 121, 1935]. 2 cc. of the irradiated solution was evaporated to dryness on a water bath. The residue was heated with a trace of tannic acid and sulphuric acid. No blue colouration was formed, while the addition of even a small trace of glycolic acid gave an intense blue colouration. This showed the absence of glycolic acid.

Besides as this reaction takes place even in the presence of tartaric, tartronic, glyceric and glyoxylic acids, the absence of these as well was presumed.

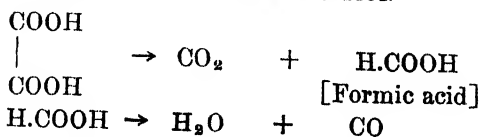
Though acetic acid is admitted as the principal product of the decomposition, no definite quantitative estimation of this acid was made. The reason is obvious. The scope of the experiments was to ascertain the decomposition of the acid into free *labile* molecules and thence to stable polymerised compounds.

From the above experiment the following conclusion was arrived at: During the photodecomposition of malonic acid various reactions take place, and stable products are formed as the effect of the photoanalysis. The following equations represent the reactions that take place:—

PRIMARY DECOMPOSITION



SECONDARY DECOMPOSITION



The decomposition products are in the following proportions:—

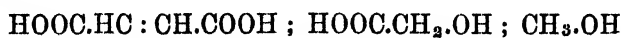
Gaseous products—

CO ₂	4.18	moles per cent.
C ₂ H ₄	0.012	moles per cent.
O ₂	0.007	moles per cent.
CO	0.073	moles per cent.
[N ₂	as impurity	0.053	moles per cent.]

In solution—

COOH					
	0.05	moles per cent.
COOH					
H.COOH	0.008	moles per cent.
H ₂ C.COOH					
	0.3	moles per cent.
H ₂ C.COOH					

The following may be discarded as among the products of decomposition :—



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[*Received July 16, 1940*]

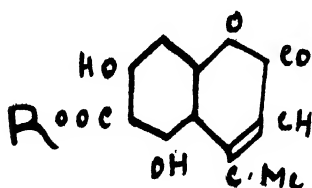
CONDENSATION OF METHYL PHLORO- GLUCINOL CARBOXYLATE WITH ETHYLACETOACETATE

By

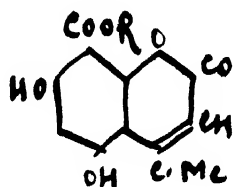
SURESH M. SETHNA

IN continuation of our previous work on the condensation of esters of phenolic acids with β -ketonic esters (J. Indian Chem. Soc., 1937, 14, 717; 1938, 15, 383; 1940, 17, 37, 211; J. C. S. 1938, 228, 1066), methyl phloroglucinol carboxylate has been condensed with ethyl acetoacetate in presence of both anhydrous aluminium chloride and concentrated sulphuric acid. The product obtained in both the cases has been found to be methyl 5-7-dihydroxy-4-methyl coumarin 6-(or 8)-carboxylate (I or II, R=Me). The constitution of the coumarin ester was proved by the hydrolysis and decarboxylation of the ester to the known 5:7-dihydroxy-4-methyl coumarin. The coumarin carboxylic acid (I or II, R=H) could not be isolated because of its unstable nature.

Phloroglucinol carboxylic acid could not be condensed with ethylacetoacetate because it readily decomposes to phloroglucinol and carbon dioxide.



(I)



(II)

EXPERIMENTAL

Phloroglucinol carboxylic acid was prepared by Skraup's method (Monatsh, 1889, 10, 724), and purified according to

Robinson and Shah (J., 1933, 612). It was esterified by diazo-methane following Herzig, Wenzel and Tolk (Monatsh, 1902, 23, 90).

METHYL 5-7-DIHYDROXY-4-METHYLCOUMARIN-6 (OR 8)
CARBOXYLATE (I OR II, R=ME)

(i) *Anhydrous aluminium chloride as condensing agent*

Methyl phloroglucinol carboxylate (2 g.) and ethyl acetoacetate (1.5 g.) were dissolved in minimum quantity of dry ether and to it a solution of anhydrous aluminium chloride (3.5 g.) in dry ether (15 c.c.) was added. The ether was gradually allowed to evaporate by heating on a warm water bath and the homogeneous mass obtained was heated in an oil bath at 120-125° for an hour when the evolution of hydrogen chloride was negligible. Dilute hydrochloric acid was added on cooling and the product obtained crystallised from rectified spirit in clusters of tiny needles (1.2 g.) m.p. 230-231°. The ester is soluble in sodium hydroxide with a deep yellow colour without any fluorescence and gives a deep violet colouration with alcoholic ferric chloride. (Found: C, 57.5; H, 3.9. $C_{12}H_{10}O_6$ requires C, 57.6, H, 4.0 per cent).

(ii) *Sulphuric acid as condensing agent*

Methyl phloroglucinol carboxylate (1.4 g.) was mixed with ethylacetoacetate (1 g.) and sulphuric acid (80%; 10 c. c.) added. After keeping for 20 hours the reaction mixture was added to cold water, and the product obtained treated with sodium bicarbonate solution to remove any acid formed. The sodium bicarbonate solution, however, yielded nothing on acidification.

The alkali insoluble portion on crystallization from rectified spirit gave clusters of tiny needles (0.9 g.) m.p. and mixed m.p. with the product from (i) was 230-31°.

The diacetyl derivative prepared as usual with sodium acetate and acetic anhydride was crystallised from rectified spirit in clusters of silky needles m.p. 161-162°. (Found: C, 57.4, H, 4.3. $C_{16}H_{14}O_8$ requires C, 57.5, H, 4.2 per cent).

The dimethyl ether prepared by refluxing the ester in acetone solution with potassium carbonate and methyl iodide was crystallised from dilute alcohol in needles, m.p. 182-183°. (Found: C, 60.5, H, 5.3. $C_{14}H_{14}O_6$ requires C, 60.4, H, 5.0 per cent).

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION
OF THE ESTER

With a view to hydrolyse the coumarin ester to the corresponding acid - 5:7-dihydroxy-4-methyl-6 (or 8) carboxylic acid (I or II, R=H), the ester (I or II, R=Me) (0.2 g.) was kept for about 40 hours with sodium hydroxide (10%; 10 c. c.). It was then acidified with hydrochloric acid. The product obtained was crystallised from dilute alcohol in pale yellow glistening needles m.p. 282-284°. Mixed m.p. with an authentic specimen of 5:7-dihydroxy-4-methyl coumarin obtained from phloroglucinol and ethyl acetoacetate (Pechmann and Cohen, Ber., 1884, 17, 2189) was not depressed.

Variations in the quantity and strength of sodium hydroxide and in the period of keeping the ester in contact with the alkali failed to give the desired acid.

The author thanks the University of Bombay for the award of a research grant.

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[Received July 17, 1940].

SOME DERIVATIVES OF CYCLOHEXANE—THE SYNTHESIS OF 1-CARBOXY CYCLOHEXANE- 1- α -SUCCINIC, 1- α -PROPIONIC, AND 1- α - BENZYLACETIC ACIDS AND OF α -CYCLOHEXYLSUCCINIC ACIDS

By

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THE cyclohexane derivatives mentioned in the title of this paper were prepared with a view to determining the best conditions for their synthesis as we wanted to prepare their alkylcyclohexane analogues for the purpose of studying their isomerism as a logical continuation of the work with which one of us (R. D. D.) has been busy for the last seven years.

1-Carboxy-cyclohexane-1- α -succinic acid (I) was prepared by the acid hydrolysis of ethyl-cyano-cyclohexane-1- α -cyanoacetate (II) which was obtained by condensing the sodioderivative of the dicyanoester (III) with ethyl bromacetate. This acid has been stated to melt at 187° by Chatterjee (J. Ind. Chem. Soc., 1937, 14, 127), while our sample melts at 206°. It is just possible that Chatterjee's sample was contaminated with some amount of 1-carboxy-cyclohexane-1-acetic acid (IV). The acid has been characterised by the preparation of its anhydride, anilic acid, anil-anilide, tolyl-toluidide and the imide, most of which are new.

1-Carboxy-cyclohexane-1- α -benzylacetic acid (V) was prepared by the benzylation of the dicyanoester (III). During the acid hydrolysis of ethyl 1-cyano-cyclohexane-1- α -benzylcyanoacetate, a considerable amount of the anhydride of (V) is formed. The acid has been characterised by its usual derivatives.

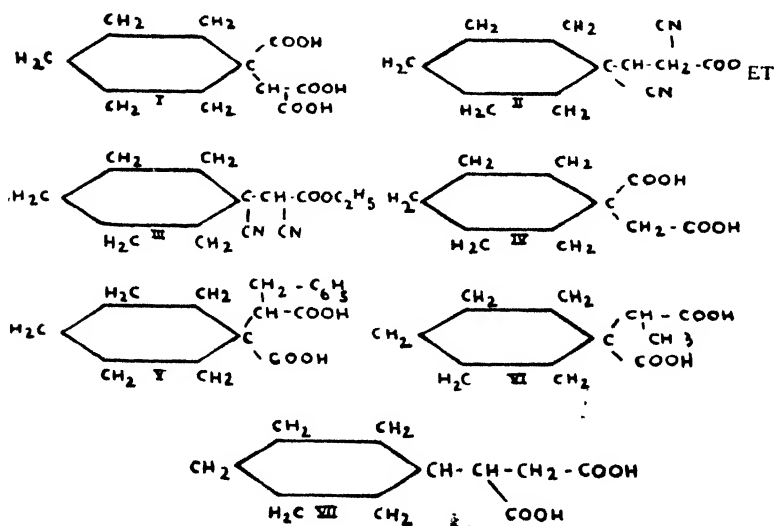
1-Carboxy-cyclohexane-1- α -propionic acid (VI) was prepared by the hydrolysis of the ester obtained by methylating the dicyanoester (III) in the presence of sodium ethoxide. The same acid has been prepared by Kandiah (J., 1932, 1215) who

gives the m.p. 110° , while our sample melts at 125° . It seems Kandiah's acid was contaminated with same impurity due to imperfect hydrolysis. We have also prepared some additional derivatives to characterise it.

It was thought interesting to prepare monosubstitution derivatives of cyclohexane in which one hydrogen is replaced by a fairly heavy acid group to see the possibility of the isomers.

With this object in view, we synthesised α -cyclohexylsuccinic acid (VII) by condensing ethyl cyclohexylcyanoacetate with ethyl bromoacetate in presence of sodium ethoxide. Acid hydrolysis of the resulting ester gave the requisite acid (VII) which was characterised by its anhydride, anilic acid and the imide. The same acid has been prepared by Ranganathan (J. Ind. Chem. Soc. 1939, 17, 107) by a slightly different method.

All these four above-mentioned acids could be isolated in only one form, and no evidence of the isomerism demanded by the armchair and boat forms of cyclohexane was encountered. It is thus necessary that at least two out of the six carbon atoms of cyclohexane should be loaded with heavy groups to establish the favourable conditions for the isolation of this type of isomers. Further work on this line on the derivatives of alkylcyclohexane has already been done, and will be published in due course.



EXPERIMENTAL

(A) *Diethyl 1-cyano-cyclohexane-1- α -cyanosuccinate*

A suspension of ethylsodiocyanoacetate ($N=4.2g.$; cyanoacetate= $24g.$; ethyl alcohol= $40cc$) was added to a solution of cyclohexanone cyanohydrin ($22g.$) in absolute alcohol with constant stirring and cooling. After allowing the mixture to stand at the ordinary temperature for 48 hours, ethylbromacetate ($32g.$) was added "in situ" in three lots, cooled, kept at the ordinary temperature for two days, and heated under reflux till the mixture was neutral. After distilling off as much of alcohol as possible, the oil precipitated on diluting the residue with water was extracted with ether, dried and distilled under reduced pressure. Three fractions were collected (1) b.p. $95-110/2mm$, (2) b.p. $110-168^{\circ}/2mm$, (3) b.p. $200-204^{\circ}/2mm$. The first fraction was rejected, while the second fraction was treated again with ethyl bromacetate in presence of sodium ethoxide. Total yield of Diethyl 1-cyano-cyclohexane-1- α -cyanosuccinate boiling at $202-204^{\circ}/2mm$ was 50 per cent. The crude ester melted at $57-61^{\circ}$, and crystallised from dilute alcohol in white plates m. p. 74° . (Found: C, 62.5; H, 7.2. calc. for $C_{16}H_{22}O_4N_2$, C, 62.8; H, 7.2 per cent.). Chatterjee (loc. cit.) describes this compound as a viscous liquid. (b.p. $200-205/7mm$).

A considerable amount which could not be distilled solidified in the claisen flask. It crystallised from petrol (b. p. 60-80) in white, lustrous laminae melting at 94° and was identified as 1-cyano-cyclohexane-1-acetonitrile, as it gave 1-carboxy-cyclohexane-1-acetic acid on hydrolysis. (Dickens, Horton and Thorpe, J, 1924, 125; 1830).

Hydrolysis of the ester to 1-carboxy-cyclohexane-1- α -succinic acid.—The ester m. p. 74° ($20g.$) which was dissolved in concentrated H_2SO_4 ($30cc$), and kept overnight, was diluted with water ($40cc$) and the mixture heated under reflux on sand-bath for 20 hours. The cooled mixture was diluted with water, saturated with ammonium sulphate, extracted with ether and purified through sodium carbonate. The crude acid which melted at $185-188^{\circ}$ was refluxed with benzene; and the benzene-insoluble portion crystallised from dilute alcohol in white plates m. p. 206° (effr). (Found: C, 54.0; H, 6.6. Calc. for $C_{11}H_{16}O_6$, C, 54.1; H, 6.5 per cent). [Chatterjee (loc. cit.) gives 187°].

The acid is soluble in alcohol, acetone, and acetic acid, but sparingly soluble in benzene and petrol. Its calcium and

barium salts are soluble while the lead and copper salts are insoluble in hot water.

The anhydride prepared by heating the dry acid in a tube at 175-180° for three hours was a viscid liquid.

The anilic acid prepared by mixing the equimolecular quantities of the anhydride and aniline in benzene solution crystallised from alcohol in small needles m. p. 132°. (Found: C, 63.6; H, 6.7. $C_{17}H_{21}O_5N$ requires C, 64.0; H, 6.6 per cent.).

The anil-anilide was obtained by heating the mixture of the acid (0.8g) and aniline (1g) at 170-175° for three hours. The resulting semi-solid mass was taken up in ether, and washed alternately with dilute HCl and ammonia, dried, recovered and crystallised from dilute alcohol when needles melting at 167° were obtained. (Found: C, 78.6; H, 6.4. $C_{23}H_{24}O_5N_2$ requires C, 74.3; H, 6.3 per cent.).

The tolyl-toluidide which was similarly prepared from the acid and p-toluidine crystallised from dilute alcohol in needles m. p. 161-162°. (Found: C, 74.1; H, 7.0. $C_{25}H_{28}O_5N_2$ requires H, 6.9 per cent.).

The imide obtained by heating the dry ammonium salt of the acid in a tube at 180° for three hours crystallised from dilute alcohol in needles m. p. 125-126°. (Found: C, 58.3; H, 6.8. $C_{11}H_{15}O_4N$ requires C, 58.7; H, 6.7 per cent.).

(B) *Preparation of Ethyl 1-cyanocyclohexane-1- α -benzyl-cyano-acetate*

This was prepared by heating for 15-16 hours the mixture of benzylchloride (25g) and sodio ethyl-1-cyanocyclohexane-1-cyanoacetate (Na=4.6g; absolute alcohol=50cc; ethylcyanoacetate=30g and cyclohexanone cyanohydrin=25g). The product worked up in the usual manner was separated into three fractions by distillation under reduced pressure (1) b.p. 90-110°/12mm, (2) b.p. 110-190°/8mm, (3) b.p. 215-220°/8mm. The first fraction was rejected, while the second fraction was treated with benzyl chloride in presence of sodium ethoxide. *The yield of ethyl-1-cyano-cyclohexane-1- α -benzyl-cyanoacetate* b.p. 220°/8mm. was 45 per cent. It solidified to a hard mass immediately and crystallised from dilute alcohol in white, lustrous needles m.p. 115°. (Found: C, 73.5; H, 7.1. $C_{19}H_{22}O_2N_2$ requires C, 73.5; H, 7.1 per cent.).

The Diamide was obtained by keeping the solution of the above ester (1g) in concentrated sulphuric acid (5cc) overnight. The solid obtained by adding the mixture to water crystallised from alcohol in white plates m. p. 215° . (Found: C, 65.5; H, 7.6. $C_{19}H_{26}O_4N_2$ requires C, 65.9; H, 7.5 per cent.).

Hydrolysis of the Ester to 1-Carboxy-cyclohexane-1- α -benzylacetic acid.—A solution of the ester (15g) in concentrated sulphuric acid (30cc) which had been kept for 12 hours was diluted with water (30cc) and heated on sand-bath under reflux for 20 hours. The cooled mixture was extracted with ether and the acidic portion extracted with sodium carbonate solution. On acidifying with concentrated hydrochloric acid, 1-carboxy-cyclohexane-1-acetic acid was precipitated as an oil which solidified immediately. The dry acid m. p. $178-180^{\circ}$ was refluxed with benzene, and the benzene-insoluble portion crystallised from dilute alcohol when needles m. p. 195° were obtained. (Found: C, 69.2; H, 7.3. $C_{16}H_{20}O_4$ requires C, 69.5; H, 7.2 per cent.).

The acid is soluble in alcohol, acetic acid, acetone and chloroform, but very sparingly soluble in benzene and petrol. Its calcium and barium salts were soluble, while the lead and copper salts were insoluble in hot water.

The anhydride obtained by heating the dry acid in a tube at $165-170$ for three hours crystallised from hexane in needles m. p. 104° . (Found: C, 74.1; H, 7.0. $C_{16}H_{18}O_3$ requires C, 74.4; H, 6.9 per cent.).

The Anilic acid prepared in benzene solution was soluble in this solvent. The solid left after the removal of the solvent was extracted with a solution of sodium bicarbonate and the alkaline solution acidified. It crystallised from dilute alcohol in white plates m. p. 177° . (Found: C, 69.6; H, 7.4. $C_{22}H_{25}O_3N + 3H_2O$ requires C, 70.0; H, 7.4 per cent.).

The Imide obtained by heating the dry ammonium salt at 180° for three hours crystallised from dilute alcohol in white needles m. p. 175° . (Found: C, 74.3; H, 7.4. $C_{10}H_{13}O_2N$ requires C, 74.7; H, 7.4 per cent.).

(C) *Preparation of Ethyl-1-cyanocyclohexane-1- α -cyanopropionate*

The sodio derivative of 1-cyanocyclohexane-1-cyanoacetate obtained by condensing cyclohexanone cyanohydrin

(13 g.) with ethyl sodio cyanoacetate ($\text{Na}=2.3$ g., absolute alcohol=30cc; ethyl cyanoacetate=12g.) was treated with methyl iodide (15g.), and kept at the room temperature for 24 hours. After warming on the water-bath till the mixture became neutral, the mixture worked up in the usual manner, and distilled under reduced pressure. The first fraction b.p. $90-120^{\circ}/6\text{mm}$ was rejected while the second fraction b.p. $130-160^{\circ}/6\text{mm}$ was remethylated on the supposition that nearly one third of the fraction was unmethylated. The final product boiled at $169^{\circ}/6\text{m.m.}$ and slowly solidified to a crystalline mass m. p. $52-54^{\circ}$. (Yield=45 per cent). (Found: C, 66.2; H, 7.5. Calc for $\text{C}_{14}\text{H}_{18}\text{O}_2$; C, 66.6; H, 7.7 per cent.).

Hydrolysis of the Ester to 1-Carboxy-cyclohexane-1- α -propionic acid.—The ester (14g.) was hydrolysed as usual with 66 per cent. H_2SO_4 (70cc) by heating on sand-bath under reflux for 24 hours, and the acid isolated and purified in the usual manner. The acid was crystallised first from hexane containing a few drops of benzene and finally from dilute alcohol when white, rectangular plates m. p. 125° were obtained. (Found: C, 59.7; H, 8.2. Calc. for $\text{C}_{10}\text{H}_{16}\text{O}_4$, C, 60.0; H, 8.0 per cent.).

It was easily soluble in alcohol, benzene, acetic acid, chloroform and acetone, while sparingly in hexane and petroleum ether. Its lead salt was insoluble in hot as well as cold water, while the copper, calcium, and barium salts were soluble. The solubility of the copper salt is particularly interesting as this property enables its purification from the impurity of 1-carboxy cyclohexane-1-acetic acid.

The *anhydride* was a liquid and was not analysed.

The anilic acid crystallised from dilute alcohol in plates m.p. $171-172^{\circ}$. [Khandiah, (loc. cit.) gives 165°]. (Found: C, 69.7; H, 7.6. Calc. for $\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$, C, 69.8; H, 7.6 per cent.).

The *p-toluidinic* acid crystallised from dilute alcohol in needles m. p. 176° . (Found: C, 70.4; H, 8.0. $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$ requires C, 66.3; H, 8.0 per cent.).

The *Imide* prepared as usual crystallised from dilute alcohol in short needles m. p. 102° . (Found: C, 66.0; H, 8.6. $\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}$ requires C, 66.3; H, 8.3 per cent.).

(D) *Synthesis of α -cyclohexysuccinic acid*

Preparation of Ethyl Cyclohexyl cyanoacetate.—Cyclohexyl bromide (32g.) was gradually added to the suspension of

ethyl sodiocyanoacetate (Na=5g. Abs. alcohol=60cc, ethyl cyanoacetate=24g.) cooled in ice, and the mixture kept at the room temperature for 48 hours. After heating on the water-bath under reflux till the solution was neutral (15 hours), most of the alcohol was distilled off; and the residue was diluted with much water. The precipitated oil was recovered as usual and distilled under reduced pressure. After rejecting the first fraction b.p. 90-120/20mm which consisted mainly of the unreacted materials, the fraction b.p. 140-160/36 m.m. was collected and redistilled when ethyl cyclohexylcyanoacetate boiled at 148-150°/20 m.m. (Yield: 60-65 per cent.) leaving a residue in the flask which could not be distilled. (Found: C, 67.5; H, 8.8. Calc. for $C_{11}H_{17}O_2N$, C, 67.8; H, 8.7 per cent.).

When hydrolysed with alcoholic caustic potash it gave cyclohexyl malonic acid m.p. 178° of Vogel (J. 1928, 2022). However, the chloroform mother-liquor from which the cyclohexylmalonic acid had crystallised out gave, on concentration, a small amount of white tiny needles m.p. 200°, and was probably the *dicyclohexyl cyanoacetic acid*. (Found: C, 71.6; H, 9.2. $C_{15}H_{23}O_2N$ requires C, 72.3 H, 92.2 percent.).

The *Di-p-toluidide* of the malonic acid m.p. 178° was prepared by heating equimolecular mixture of the acid and aniline at 170° for 4 hours. After washing the residue alternately with dilute HCl and ammonia the di-*p*-toluidide crystallised in tiny needles m.p. 128-129°. (Found: C, 76.5; H, 7.7. $C_{23}H_{28}O_2N_2$ requires C, 75.8; H, 7.7 per cent.).

Preparation of Diethyl α -cyano- α -cyclohexyl-succinate.—Ethyl bromacetate (13g) was slowly added to a suspension of ethyl sodio-cyclohexylcyanoacetate (Na=1.9g; ester=16g; abs. alcohol 30CC. The mixture was heated for 18 hours after allowing to remain at the ordinary temperature for two days. On working up as usual, the liquid was distilled under reduced pressure when after the removal of some low-boiling fraction, the resulting product boiled at 195-198/18 m.m. (Yield 12g). (Found: C, 63.7; H, 8.3. $C_{15}H_{23}O_4N$ requires, C, 64.0; H, 8.1 per cent.).

Hydrolysis of the ester to α -cyclohexyl-succinic acid.—The above ester (10 g.) was hydrolysed as usual with 66 per cent. H_2SO_4 (40 c.c.), and worked up as usual for the acid. The crude acid m.p. 139-142° was refluxed with hexane, and the insoluble solid recrystallised from benzene, when white plates m.p. 150° were obtained. [Ranganathan, (loc. cit.) gives 145°].

(Found: C, 59·5; H, 7·9. Calc. for $C_{10}H_{16}O_4$, C, 60·0; H, 8·0 per cent.).

Its calcium and barium salts are soluble, while lead and copper salts are insoluble in water.

The anhydride prepared by heating the dry acid at 170° for three hours crystallised from hexane in white, needles m.p. $41-42^\circ$. [Ranganathan (loc. cit.)].

The anilic acid prepared as usual in benzene solution crystallised from dilute alcohol in needles; m.p. 192° . (Found: C, 69·7; H, 7·9. $C_{16}H_{21}O_3N$ requires C, 69·8; H, 7·6 per cent.).

The Imide prepared by heating the dry ammonium salts at 180° for three hours crystallised from dilute alcohol in tiny needles m.p. 164° . (Found: C, 63·2; H, 8·9. $C_{10}H_{15}O_2N$ requires C, 63·1; H, 8·4 per cent.).

This work was carried out at the Muslim University, Aligarh, and we take this opportunity of thanking Capt. M. Haider Khan, M.A. (Oxon), B.Sc. (Lond.), for the interest he showed in the work, and the provision of the facilities.

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ACTION OF THIONYL CHLORIDE, SULPHUR DICHLORIDE AND SULPHUR MONOCHLORIDE ON NAPHTHOL DERIVATIVES

By

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THE present investigation is in continuation of a similar investigation on salicylic acid and its esters, communicated through this Laboratory (Kundergi, Chakradev and Shah, *Current Science*, vol. 5, Oct., 1936, 198; *J. Univ. Bom.*, vol. 6, Sept., 1937, 82).

In the present investigation certain derivatives of naphthol were selected to see how far the substitution of the benzene ring by the naphthalene ring brought about a change in the course of the reaction.

2-acetyl- α -naphthol; β -naphthol; 1:2 oxynaphthoic acid; and 2:3 oxynaphthoic acid were selected for the investigation.

2-acetyl- α -naphthol, only in the presence of catalysers, gave, both with thionyl chloride and sulphur dichloride, the same product:—3,3'-diacetyl-4,4'-dihydroxy-dinaphthyl sulphide.

But with sulphur monochloride, it gave a compound which seems to contain three sulphur atoms. The two additional sulphur atoms seem to be loosely bound, since on acetylation the same acetyl derivative as that of 3,3'-diacetyl-4,4'-dihydroxy-dinaphthyl sulphide, is formed. The formation of this compound can be explained on the assumption that under certain conditions sulphur monochloride acts as if it were a mixture of SCl_2 and S_2Cl_2 (Richter, *Ber.*, 49. 1024).

β -naphthol, in the presence of a catalyser, both with sulphur dichloride and with sulphur monochloride gave the same product 2,2'-dihydroxy-dinaphthyl sulphide.

With thionyl chloride, under similar conditions, β -naphthol gave only a plastic mass.

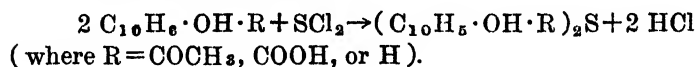
1:2 oxynaphthoic acid was allowed to react, in the presence of a catalyser, with sulphur dichloride, when it gave *3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl sulphide*.

But with sulphur monochloride, under similar conditions, it gave *3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl disulphide*.

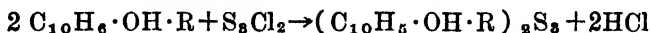
2:3 oxynaphthoic acid, in the presence of a catalyser, with sulphur dichloride as well as with sulphur monochloride gave the same product:—*2,2'-dihydroxy-3,3'-dicarboxy-dinaphthyl sulphide*.

With thionyl chloride, under similar conditions, both the acids failed to react and only the original acids were recovered.

The reaction between sulphur dichloride on the one hand and 2-acetyl- α -naphthol, β -naphthol, and the two acids on the other, can be represented thus:—

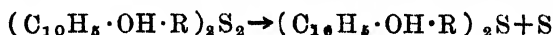
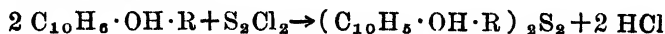


The reaction between sulphur monochloride and 2-acetyl- α -naphthol can be explained as under:—



Similarly the reaction between 1:2 oxynaphthoic acid and sulphur monochloride can be explained as under:—

$2 \text{C}_{10}\text{H}_8 \cdot \text{OH} \cdot \text{R} + \text{S}_2\text{Cl}_2 \rightarrow (\text{C}_{10}\text{H}_8 \cdot \text{OH} \cdot \text{R})_2\text{S}_2 + 2 \text{HCl}$,
whereas the reaction between β -naphthol and sulphur monochloride on the one hand and 2:3 oxynaphthoic acid and sulphur monochloride on the other, can be explained by presuming that first of all a disulphide is formed, which subsequently loses one sulphur atom as under:—



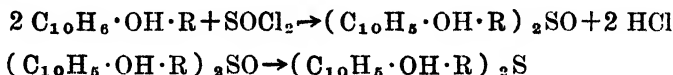
This view point is supported by the fact that sulphur is deposited during the course of the reaction.

Incidentally, the formation of the disulphide and the easy removal of the sulphur atom from the same, supports the view that the structure of sulphur monochloride is Cl—S—Cl



No other explanation for the reaction between thionyl chloride and 2-acetyl- α -naphthol can be given except that first

of all a sulphoxide is formed which oxidises the reacting substances, itself being reduced to the thioether. This explains the smaller yield of the thioether when thionyl chloride is used :—



This view (about the formation of a sulphoxide) is supported by the researches of Colby and McLoughlin (*Ber.*, 20, 195), and S. Smiles and co-workers (*J. C. S.*, 1906, 696; *J. C. S.* 1907, 1118; and *J. C. S.*, 1910, 2249).

The constitution of the compounds was proved by acetylation, nitration and bromination. Ferric chloride reaction indicated and acetylation proved the presence of two hydroxyl groups in the molecule. Bromination in the case of 2,2'-dihydroxy-dinaphthyl sulphide, and nitration in the rest of the cases gave rise to a bromo-derivative and nitro-derivatives, respectively, of the original compounds. The position occupied by the bromine atom or by the nitro-group must naturally be the position where sulphur linking must have taken place. As a result of the nitration or bromination of the thioethers, only a single nitro or bromo-derivative was obtained in each case. In no case were we able to isolate more than one such derivative. This proves the symmetrical nature of the molecule.

Thus the thioethers of 2-acetyl- α -naphthol, β -naphthol, 1:2 oxynaphthoic acid, and 2:3 oxynaphthoic acid gave respectively, the following acetyl derivatives :—

3,3'-diacetyl-4,4'-diacetoxy-dinaphthyl sulphide,
2,2'-diacetoxy-dinaphthyl-sulphide,
3,3'-dicarboxy-4,4'-diacetoxy-dinaphthyl sulphide, and
2,2'-diacetoxy-3,3'-dicarboxy-dinaphthyl sulphide.

Secondly, they gave, respectively, the following nitro- or bromo-compounds :—

2-acetyl-4-nitro- α -naphthol (Friedlaender, *Ber.*, 28, 1948),
1-bromo-2-naphthol (Smith, *J. C. S.*, 35, 789),
2:4-dinitro- α -naphthol (König, *Ber.*, 25, 806), and
3-hydroxy-4-nitro-2-naphthoic acid (Robertson, *J. Praktische Chemie*, 2, 48, 534).

These results obtained by us are in conformity with the usual conclusions which one would arrive at on theoretical grounds also, i.e., the incoming sulphur atom should occupy a

position para or ortho to the $-OH$ group and meta to the $-COOH$ or $-COCH_3$ groups. Similarly our conclusions regarding the position of this sulphur atom fall in line with those arrived at by Hirve, Jadhav and Chakradev (*J. Univ. Bom.*, 1933, 128; *J. Ind. Chem. Soc.* 1934, 551; *J. Am. Soc.*, 1935, 101) as well as by S. Smiles (*J. C. S.*, 1907, 1118) who worked with benzene derivatives. Further in the case of β -naphthol the conclusion arrived at by us regarding the position of the sulphur atom is in conformity with the views expressed by Fieser and Lothrop (*J. Am. Soc.*, 57, 1459-1464).

The $-OH$ group by itself is very reactive, so that in the case of α -naphthol the reaction with sulphur dichloride is very vigorous. Only when inhibited by the presence of a carboxyl group or by $-COCH_3$ group in the ortho position or by the para position being occupied, the reaction is brought under control.

It is interesting to note that though the thio-compounds formed, retain the $-OH$ group, they refuse to react with metallic sodium or potassium. This must naturally be due to the less positive character of the $-H$ atom of the $-OH$ group.

EXPERIMENTAL

(The experimental part of this work is carried out by
Mr. Airan alone. — S. V. S.)

3,3'-diacetyl-4,4'-dihydroxy-dinaphthyl sulphide (I)

2-acetyl- α -naphthol (10 gm) was dissolved in benzene, and thionyl chloride (5 gm) was added to it. The mixture was kept in a conical flask provided with a glass tube in a tight fitting cork, the tube itself being drawn out into a fine capillary to keep out moisture. The reaction took place with the evolution of hydrochloric acid gas. A good deal of thionyl chloride was swept away by the hydrochloric acid fumes. Next day the benzene was distilled off, and the residue was dissolved in chloroform. It was not easy to obtain the compound free from free sulphur, and the yield hardly exceeded 20 percent. The solid obtained was yellow, crystalline, m. p. $200^\circ C$. Zinc chloride and bismuth chloride were separately used as catalysers.

Later, instead of thionyl chloride sulphur dichloride was used under similar conditions as above, and an identical yellow crystalline substance fell out after 24 hours, m.p. $200^\circ C$; mixed m.p. with the compound (I), $200^\circ C$. The same catalysers were

used. The yield was now 55 per cent. But yet repeated recrystallizations were required to free the compound of free sulphur and to obtain it in pure condition. The new compound is insoluble in ether, whereas not only 2-acetyl- α -naphthol, but also free sulphur is soluble in ether. Hence on using ether as a medium the yield went upto 80 per cent., and more.

There was yet another development: the reaction product was removed by filtration, and the same ethereal mother liquor was used over again by adding the reacting substances in any proportions, sulphur dichloride, of course, being always in excess. Now the product fell out within an hour. Thus the used mother liquor increased the speed of the reaction.

The compound is insoluble in water, ether, and in alcohol, but is soluble in chloroform, hot benzene and hot toluene. It goes into solution in alkali, and can be reprecipitated by dilute hydrochloric acid. It gave the ferric chloride reaction for hydroxyl group :—

	Found per cent.	$C_{24}H_{18}O_4S$ requires
0.1574 gm gave 0.08949 gm $BaSO_4$	7.98 S	8.0
4.807 mgm gave 12.485 mgm CO_2	70.88 C	71.64
4.807 mgm gave 1.96 mgm H_2O	4.46 H	4.48

3,3'-diacetyl-4,4'-diacetoxy-dinaphthyl sulphide (II)

The substance was dissolved by warming in acetic anhydride and was refluxed on the wire gauze for about 10 hours. After cooling it was poured over crushed ice, and left over night. It was then washed, filtered, and crystallized from alcohol, m. p. $176^\circ C$. It was whitish, and was insoluble in dilute sodium hydroxide. It gave no ferric chloride reaction for hydroxyl group :—

	Found per cent.	$C_{28}H_{22}O_6S$ requires
0.17 gm gave 0.0787 gm $BaSO_4$	6.362 S	6.585
4.298 mgm gave 10.905 mgm CO_2	69.22 C	69.13
4.298 mgm gave 1.79 mgm H_2O	4.66 H	4.52

Refluxing with an excess of decinormal KOH solution, and backtitrating with standard HCl, the equivalent weight was

found as under :—

0.3801 gm substance required 0.0936 gm KOH.

Equivalent weight found 227.3

That required theoretically, presuming that
there are two acetoxy groups 243.0

*Nitration of 3,3'-diacetyl-4,4'-dihydroxy-dinaphthyl
sulphide (III)*

To a mixture of 5 gm of the substance in 20 cc of glacial acetic acid was added a mixture of 1.5 cc of concentrated nitric acid in about 3 cc of glacial acetic acid. It was well shaken. Within a few minutes a yellow substance fell out. The whole was then poured in cold water and filtered. It was then washed with ether (after drying) to remove free sulphur, if any, and was recrystallized from alcohol, m.p. 154-155°C. Mixed m.p. with the known nitro compound prepared by us in the laboratory (m.p. 155°C) from 2-acetyl- α -naphthol, was 155°C. It gave the ferric chloride reaction for hydroxyl group.

3,3'-diacetyl-4,4'-dihydroxy-dinaphthyl trisulphide (IV)

2-acetyl- α -naphthol (10 gm) was dissolved in ether, and sulphur monochloride (4 gm) was added in the manner adopted in the case of the reaction with sulphur dichloride. Zinc chloride was used as a catalyser. A yellow substance fell out, m.p. 191-192°C, mixed m.p. with the compound I, 180°C :—

	Found per cent.	$C_{24}H_{18}O_4S_3$ requires
0.1904 gm gave 0.2845 gm $BaSO_4$	20.53 S	20.6

Acetyl derivative of the above compound (V)

The compound was refluxed for 10 hours with acetic anhydride and then after cooling was poured over crushed ice and left over night. It was recrystallized from alcohol, m.p. 175°C, mixed m.p. with compound II, 175°C :—

	Found per cent.	$C_{28}H_{22}O_6S$ requires
0.1554 gm gave 0.0764 gm $BaSO_4$	6.756 S	6.585

2,2'-dihydroxy-dinaphthyl sulphide (VI)

β -naphthol (10 gm) was dissolved in ether and sulphur dichloride (5 gm) was added, the entire arrangement being as in

the case of 2-acetyl- α -naphthol. Zinc chloride was used as a catalyser. A whitish substance fell out within an hour, and the mother liquor was used over again as in the previous case. The substance was recrystallized from alcohol, m.p. 212°C. Instead of ether, benzene was used as a medium with success. The substance is soluble in hot alcohol with difficulty, but insoluble in water, ether, or benzene. It gave the ferric chloride reaction for hydroxyl group. It was white and crystalline :—

	Found per cent.	$C_{20}H_{14}O_2S$ requires
0.1018 gm gave 0.0766 gm $BaSO_4$	10.34 S	10.07

2,2'-diacetoxy-dinaphthyl sulphide (VII)

2,2'-dihydroxy-dinaphthyl sulphide was suspended in excess of acetic anhydride and refluxed for a couple of hours, and then after cooling, was poured over crushed ice and left over night. It was then filtered, washed and recrystallized from alcohol, m.p. 198°C. It gave no ferric chloride reaction :—

	Found per cent.	$C_{24}H_{18}O_4S$ requires
0.20 gm gave 0.117 gm $BaSO_4$	8.039 S	7.96

Bromination of 2,2'-dihydroxy-dinaphthyl sulphide (VIII)

The substance (10 gm) was suspended in 75 cc of glacial acetic acid, and to this mixture was added through a dropping funnel, drop by drop, a mixture of 10 gm bromine in about 7 cc of glacial acetic acid. The flask was held in a trough containing cold water and was shaken thoroughly at each addition. It was then left overnight in that water bath. Next day it was filtered and to the filtrate was added an aqueous solution of a few crystals of sodium thiosulphate to remove free bromine, because it was observed that this free bromine later on hindered the purification of the bromo-compound. Then it was diluted with water, and the substance that fell out was filtered and washed. It was chocolate in colour, and was evidently in an impure condition. It was then dissolved in benzene and allowed to crystallize, but the compound even after five such recrystallizations remained a little impure. Then it was dissolved in alcohol and a few crystals of sodium thiosulphate were again added, and then the alcoholic solution was diluted with water till a white substance fell out. It was finally recrystallized from benzene,

when white needles were obtained, m. p. 83°C , mixed m. p. with 1-bromo-2-naphthol which was prepared by us in the laboratory (m.p. 83°C) was 83°C . The method adopted by us in the purification of the compound is an improvement on the one adopted by Smith (*J. C. S.* 35, 789):—

	Found per cent.	$\text{C}_{10}\text{H}_7\text{OBr}$ requires
0.1582 gm gave 0.1314 gm AgBr	35.34 Br	35.84

β -naphthol treated with sulphur monochloride (IX)

β -naphthol (10 gm) was dissolved in ether and sulphur monochloride was added in the manner adopted in previous cases. Zinc chloride was used as a catalyser. A white substance fell out within an hour. It was recrystallized from alcohol, m.p. 212° mixed m.p. with compound VI, 212°C :—

	Found per cent.	$\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}$ requires
0.1610 gm gave 0.1163 gm BaSO_4	9.936 S	10.97

Acetyl derivative of the above compound (X)

The acetyl derivative was prepared in the usual manner m.p. 194°C , mixed m.p. with compound VII, 196°C .

3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl sulphide (XI)

1:2 oxynaphthoic acid (10 gm) was dissolved in ether and sulphur dichloride (5 gm) was added in the manner adopted in previous cases. The mother liquor was used over again. The new compound fell out within an hour in the first instant, and then even earlier, m. p. $265\text{--}267^{\circ}\text{C}$. It is insoluble in water, ether, acetone, benzene, toluene, carbon tetrachloride, and very slightly soluble in alcohol. It was greyish white and amorphous. It gave ferric chloride test for hydroxyl group:—

	Found per cent.	$\text{C}_{22}\text{H}_{14}\text{O}_6\text{S}$ requires
0.10 gm gave 0.0611 gm BaSO_4	8.395 S	7.881

On dissolving the substance in an excess of decinormal KOH solution, and back-titrating with standard HCl, the equivalent weight was found out as follows:—

0.0985 gm substance required 0.0260 gm KOH.

Equivalent weight found 211.8
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That required theoretically presuming that there

are two carboxyl groups 206
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3,3'-dicarboxy-4,4'-diacetoxy-dinaphthyl sulphide (XII)

It was prepared in the usual manner by refluxing for about 4 hours. It was recrystallized from chloroform, m.p. 150-151°C. It gave no ferric chloride test for hydroxyl group :—

	Found per cent.	$C_{20}H_{12}O_6S$ requires
0.1376 gm gave 0.063 gm $BaSO_4$	6.30	6.53

The equivalent weight was found out by dissolving the substance in an excess of decinormal KOH solution, and back-titrating with standard HCl, as follows :—

0.1292 gm substance required 0.0307 gm KOH.

Equivalent weight found 235.6

That required theoretically, presuming that
there are two carboxyl groups 245.0

By refluxing the substance with an excess of decinormal KOH solution, and back-titrating with standard HCl, the acetyl estimation was done as under :

0.177 gm substance required 0.0767 gm KOH.

Equivalent weight found 129.1

That required theoretically, presuming there
are two carboxyl groups in addition to two
acetoxy groups 122.5

Nitration of 3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl sulphide (XIII)

To a mixture of 2 gm of the compound in 50 cc of glacial acetic acid was added a mixture of 3 cc concentrated nitric acid in glacial acetic acid. It was then gently warmed to start the reaction. After the reaction was over, the mixture was allowed to cool, and was then poured over crushed ice. The solid that separated out was shaken with sodium bicarbonate and filtered. The residue was recrystallized from alcohol, m.p. 137°C; mixed m.p. with the 2:4-dinitro- α -naphthol (m.p. 137°C) prepared by us in the laboratory, was 137°C.

Barium salt of 3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl sulphide (XIV)

A little water was added to 3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl sulphide, and then a very little excess of ammonia. Then the solution was slightly warmed, and a warm solution of

barium chloride was added, when a precipitate was formed. This was filtered, washed and again shaken with a little ammonia to remove any unacted upon original compound. Finally, it was washed with ether. It had greyish appearance :—

	Found per cent.	$C_{22}H_{12}O_6BaS$ requires
0.1176 gm gave 0.0532 gm $BaSO_4$	25.43 Ba	25.32

Calcium salt of 3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl sulphide (XV)

It was prepared and purified in the same manner as the barium salt, by adding a warm solution of calcium chloride. It had greyish appearance :—

	Found per cent.	$C_{22}H_{12}O_6CaS$ requires
0.1856 gm gave 0.0556 gm $CaSO_4$	8.812 Ca	9.010

3,3'-dicarboxy-4,4'-dihydroxy-dinaphthyl disulphide (XVI)

1:2 oxynaphthoic acid (10 gm) was dissolved in ether and sulphur monochloride (4.1 gm) was added to it in the manner already adopted in previous cases. Zinc chloride was used as a catalyser. Here also the mother liquor was used over again. A yellowish grey substance fell out, which was then washed with ether and alcohol, m.p. 259-260°C, mixed m.p. with compound XI, was 260°C. It gave ferric chloride test for hydroxyl group :—

	Found per cent.	$C_{22}H_{14}O_6S_2$ requires
0.15 gm gave 0.1595 gm $BaSO_4$	14.62 S	14.61

Acetyl derivative of the above compound (XVII)

It was prepared in the same manner as the compound XII, and was identical in appearance and properties with that compound. It was crystallized from chloroform, m.p. 150-152°C, mixed m.p. with compound XII, was 150°C. It gave no ferric chloride reaction for hydroxyl group.

2,2'-dihydroxy-3,3'-dicarboxy-dinaphthyl sulphide (XVIII)

2:3 oxynaphthoic acid (10 gm) was dissolved in ether and sulphur dichloride (5 gm) was added to it in the usual manner. The mother liquor was used over again. The substance was very slightly soluble in acetone, alcohol, chloroform, and carbon-tetrachloride. It was recrystallized from a mixture of acetone

and carbon tetrachloride, m.p. 285°C . It gave the ferric chloride test for hydroxyl group :—

	Found per cent.	$\text{C}_{22}\text{H}_{14}\text{O}_6\text{S}$ requires
0.11 gm gave 0.0639 gm BaSO_4	7.982 S	7.881

The equivalent weight was found by dissolving the substance in excess of decinormal solution of KOH and back-titrating with standard HCl :—

0.0944 gm substance required 0.0251 gm KOH

Equivalent weight found 210.8

That required theoretically, presuming there
are two carboxyl groups 206.0

2,2'-diacetoxy-3,3'-dicarboxy-dinaphthyl sulphide (XIX)

It was prepared in the usual manner, and was recrystallized from alcohol, m.p. $305\text{--}306^{\circ}\text{C}$. It gave no ferric chloride reaction for hydroxyl group :—

	Found per cent.	$\text{C}_{26}\text{H}_{18}\text{O}_8\text{S}$ requires
0.1518 gm gave 0.0756 gm BaSO_4	6.842 S	6.53

The equivalent weight was found out by dissolving the substance in excess of decinormal KOH solution, and back-titrating with standard HCl :—

0.1027 gm substance required 0.0246 gm KOH.

The equivalent weight found 233.8

That required theoretically, presuming there
are two carboxyl groups 245.0

On refluxing the substance with an excess of decinormal KOH solution, and back-titrating with standard HCl :—

0.1064 gm substance required 0.051 gm KOH.

Equivalent weight found 116.8

That required theoretically, presuming there
are in addition two acetoxy groups 122.5

Nitration of 2,2'-dihydroxy-3,3'-dicarboxy-dinaphthyl sulphide (XX)

To a mixture of 2 gm of the substance in 50 cc of glacial acetic acid was added a mixture of 4 cc of concentrated nitric acid in glacial acetic acid. It was then gently warmed over the

flame to start the reaction. When the reaction was over, the whole was poured over crushed ice and left over night. Then it was filtered, washed, and recrystallized from alcohol, m.p. 233-238°C, mixed m.p. with the 4-nitro-3-hydroxy-2-naphthoic acid (m.p. 235-238°C) prepared by us in the laboratory, was 237°C.

Barium salt of 2,2'-dihydroxy-3,3'-dicarboxy-dinaphthyl sulphide (XXI)

The barium salt was prepared in exactly the same manner as compound XIV. It was yellowish :—

	Found per cent.	$C_{22}H_{12}O_6BaS$ requires
0.129 gm gave 0.0560 gm $BaSO_4$	25.56 Ba	25.32

Calcium salt of 2,2'-dihydroxy-3,3'-dicarboxy-diraphthyl sulphide (XXII)

This was prepared in the same manner as compound XV. It was yellow :—

	Found per cent.	$C_{22}H_{12}O_6CaS$ requires
0.1416 gm gave 0.0430 gm $CaSO_4$	8.933 Ca	9.010

2:3 oxynaphthoic acid treated with sulphur monochloride (XXIII)

2:3 oxynaphthoic acid (10 gm) was dissolved in ether and sulphur monochloride (4.1 gm) was added to it. Zinc chloride was used as a catalyser. The entire arrangement was similar to that adopted in previous case, and the mother liquor was used over again. A yellow substance fell out. It was washed and recrystallized from a mixture of acetone and carbon tetrachloride, m.p. 280°C. Mixed m.p. with compound XVIII was 280°C. It gave the ferric chloride test for hydroxyl group :—

	Found per cent.	$C_{22}H_{14}O_6S$ requires
0.1533 gm gave 0.0860 gm $BaSO_4$	7.709 S	7.881

One of us (S. V. S.) takes this opportunity to thank the University of Bombay for a research grant which enabled this piece of work to be done.

CHEMISTRY OF β -ARYL GLUTACONIC ACIDS

PART VI: *C-Benzoylation of β -aryl glutaconic anhydrides and thermal decarboxylation of C-acyl- β -aryl glutaconic anhydrides*

By

G. R. GOGTE

IN a recent publication¹, Bhave has tried to argue in support of the glutaconyl acetic acid structure² for the α -C-acetyl- β -aryl-glutaconic anhydrides described by Gogte.³ It is worth recalling, therefore, that the series of observations made in this laboratory and which support the α -C-acetyl-anhydride structure in place of the glutaconyl-acetic acid one, *e.g.*, in the typical case of the α -C-acetyl derivative—m.p. 132°C—of β -4-methoxy-phenyl-glutaconic anhydride are as follows :—

- (1) The synthesis of the compound, m.p. 133°, from the glutaconic anhydride by Einhorn's method.
- (2) The decomposition of the compound, m.p. 132°C, by aniline into acetanilide and β -4-methoxy-phenyl-glutaconic acid-semianilide.⁴
- (3) The decomposition of the compound, m.p. 132°C, by water to produce the ketonic acid, m.p. 125°C.
- (4) The action of hydrochloric acid on the compound, m.p. 132°C, to give β -4-methoxyphenyl-propylene.
- (5) The action of alcohol on the compound, m.p. 132°C, to produce an acid ester, m.p. 138°C, and a lactonic ester, m.p. 106°C, and the transformation of these compounds into the known β -4-methoxyphenyl-glutaconic acid and *p*-methoxy-cinnamic acid.

1. Bhave, *Rasayanam*, 1938, 1, 127.
2. Limaye and Bhave, *J. Univ. Bom.*, 1933, 2, 82.
3. Gogte, *Proc. Ind. Acad. Sci. (A)*, 1938, 7, 214.
4. Compare, Thole and Thorpe, *J. C. S.*, 1911, 99, 2217.

- (6) The isomeric transformation of the C-acetyl-anhydride, m.p. 132°C, by dilute sulphuric acid into the lactonic acid, m.p. 181°C, and the identity of the ethyl ester of this isomer with the lactonic ester, m.p. 106°C, described above.
- (7) The further acetylation of the α -C-acetyl-glutaconic anhydrides to give $\alpha\gamma$ -C-diacetyl-glutaconic anhydrides.⁵

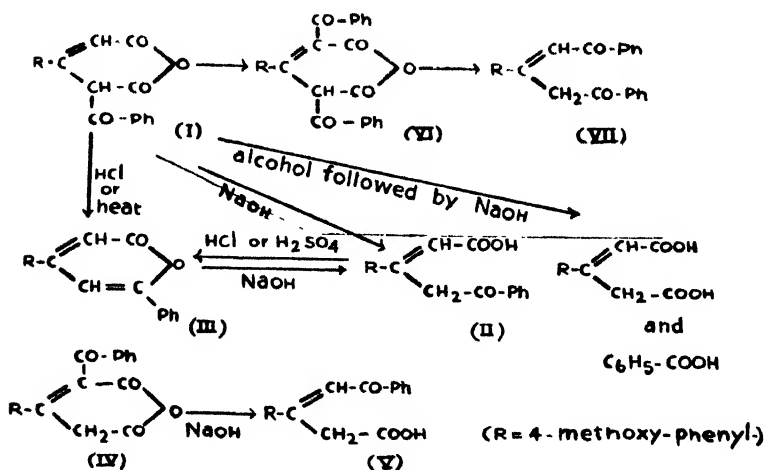
In attempting to explain the reaction (1) on the basis of a glutaconyl-acetic acid structure, Bhavé quotes some examples⁶ of the condensation of aromatic aldehydes with acid chlorides being accomplished by bases as pyridine to proceed according to Perkin's reaction, but usually the yields of the products are very poor in these cases. Bhavé has, however, failed to point out a single example where, instead of a far more reactive aromatic aldehyde, an anhydride of a dibasic acid has been condensed with acid chlorides in this way to give compounds of the phthalyl-acetic acid type (Gabriel's reaction). Apart from this, Bhavé has, strangely enough, overlooked the rest of the above mentioned factual observations which can only be explained on the basis of a α -C-acetyl-glutaconic anhydride structure, and which cannot definitely be explained on the basis of a glutaconyl-acetic acid constitution. Bhavé's chief argument in support of the glutaconyl acetic acid structure as against the α -C-acetyl glutaconic anhydride structure, and which might have led him into ignoring the above mentioned reactions, appears to be the thermal decarboxylation of the compounds in question to produce the lactones (III). Before advancing any explanation for this reaction on the basis of a α -C-acetyl-glutaconic anhydride structure, it was thought advisable to see whether β -aryl-glutaconic anhydrides could be C-benzoylated to give acidic benzoyl derivatives and whether these compounds also give this reaction. For such acidic benzoylated anhydrides will necessarily have only the α -C-benzoyl-glutaconic anhydride structure, no alternative structure such as the glutaconyl acetic acid being possible in this case.

β -Aryl glutaconic anhydrides have been found to get benzoylated easily by Einhorn's method to produce acidic compounds giving colouration with ferric chloride. The β -4-methoxyphenyl-glutaconic anhydride gave two compounds, m.p. 119°C and 194°C, according to the experimental

5. Gogte, Ind. Sci. Cong. Abstr., 1938, p. 57; J. Univ. Bom., 1939, 8, 208.

6. Chem. Zentr., 1934, I, 2411; 1936, I, 2324.

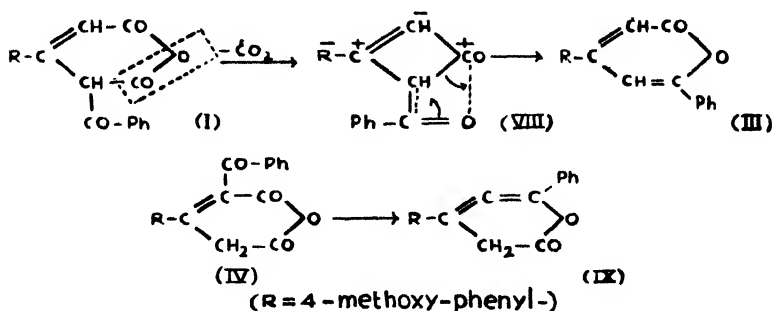
conditions. The compound m.p. 119°C , must have the structure of α -C-benzoyl- β -4-methoxyphenyl-glutaconic anhydride (I) for just as the corresponding α -C-acetyl anhydride,⁸ it gives with alkalis a ketonic acid, m.p. 114°C (II) and this ketonic acid gives a lactone, m.p. 145°C (III) with hydrochloric or sulphuric acid. This lactone is also produced by the action of hydrochloric acid on the C-benzoyl anhydride, m.p. 119°C , and is converted back into the ketonic acid, mp. 114°C , by alcoholic alkali.⁹ Also by the successive actions of absolute alcohol and caustic alkali, the C-benzoyl anhydride, m.p. 119°C , gets decomposed into the β -4-methoxy phenyl-glutaconic acid and benzoic acid. In the case of C-benzoylation, the substitution of the α -position in the glutaconic anhydride is established conclusively as the α -C-benzoyl anhydride (I) only can give a ketonic acid (II) capable of giving a lactone (III). The alternative γ -C-benzoyl-anhydride (IV) will give a ketonic acid (V) which cannot give a lactone. In fact when $\text{R} = \beta$ -(2-methoxy-5-methyl-phenyl), ketonic acids of similar structure (V) are known, but they are stable towards hydrochloric acid, and are converted into the indene-acetic acids by sulphuric acid.⁷ The other compound, m.p. 191°C , is evidently the $\alpha\gamma$ -C-dibenzoyl- β -4-methoxy-phenyl-glutaconic anhydride (VI) as it is obtained by further benzoylating the α -C-benzoyl-anhydride (I) and gives a diketone (VII) by the action of caustic alkali. The benzoyl residue in these benzoyl anhydrides appears to be more tenaciously held as they gave no propylene derivatives by hydrochloric acid.



Now just as in the case of the α -C-acetyl-glutaconic anhydrides, the α -C-benzoyl-glutaconic anhydrides (I) also lose carbon-dioxide at their melting points to produce the lactones (III), and any explanation offered for this decomposition holds good in the case of the C-acetyl anhydrides also. Some anhydrides of dibasic acids are known to lose carbon-dioxide when heated to high temperatures and produce ketones.⁸ The α -C-benzoyl anhydride (I) being an anhydride of a ketonic acid will lose carbon-dioxide more easily to produce a cyclic ketone (VIII). This compound, having a ketonic group and a double bond in a four membered ring, is extremely unstable and isomerises to the lactone (III) having a stable pyrone ring with a strong conjugation. This isomerism is only a special case

of the $\begin{array}{ccc} \text{H} & & \text{H} \\ & \diagdown \quad \diagup & \\ \text{O}=\text{C}-\text{C} & \rightarrow & \text{O}-\text{C}=\text{C} \end{array}$ isomerism where instead of

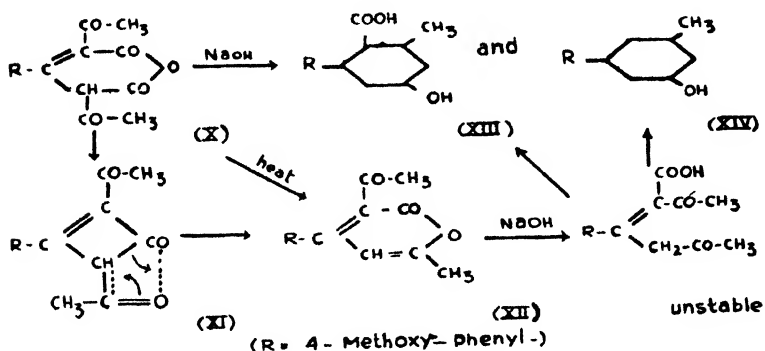
the bond between hydrogen and carbon, that connecting the ketonic carbon and α -carbon atom in the ring changes its position and connects this ketonic carbon to the oxygen of the carbonyl group outside the ring, with the consequent shifting of the C=O double bond to C=C. Incidentally this reaction is characteristic of only the α -acyl anhydrides, as a γ -benzoyl anhydride (IV) will give a lactone (IX) containing a carbon atom attached to two double bonds.



The $\alpha\gamma$ -C-dibenzoyl and $\alpha\gamma$ -C-diacetyl glutaconic anhydrides (X) also decompose similarly to give lactones of the type (XII) evidently through the unstable ketone (XI), the alternative isomerisation of this ketone being impossible as the resulting lactone will be like (IX). This lactone (XII) would give a hydroxy-diphenyl (XIV) and a hydroxy-diphenyl-

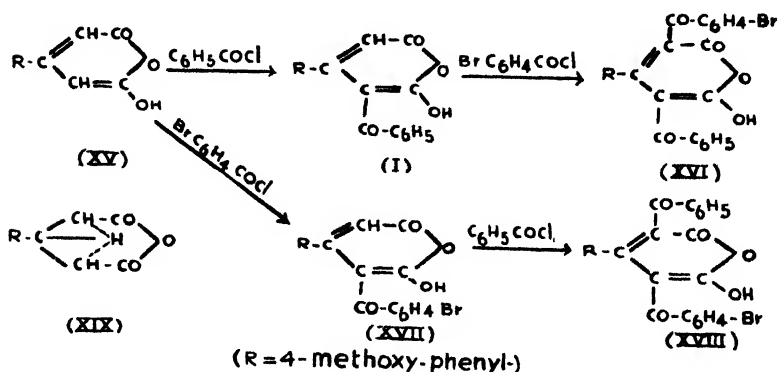
8. Blanc, *Compt. Rend.*, 1907, 144, 1356; Grabe and Mensching, *Ber.*, 1880, 13, 1303; Grabe and Aubin, *Annalen*, 247, 265.

carboxylic acid (XV) which must be a para-hydroxy acid. This is, therefore, a direct method of differentiating between the ortho-hydroxy and para-hydroxy structures for the acids obtained by the action of caustic alkalis on the $\alpha\gamma$ -C-diacetyl- β -aryl-glutaconic anhydrides.⁵ The former method of comparing with salicylic acid which gives a phenyl ester-salol-by thermal decomposition is only an indirect one.⁵ Thus the $\alpha\gamma$ -diaceto- β -4-methoxyphenyl-glutaconic anhydride, m.p. 108°C (X) on thermal decarboxylation gave a lactone, m.p. 111°C (XII) which with caustic alkalis gave the hydroxy-diphenyl-carboxylic acid, m.p. 182°C and the hydroxy-diphenyl, m.p. 118°C (XXIV). Hence the acid m.p. 182°C must have the para-hydroxy structure (XIII) and not the ortho-hydroxy as stated before.⁵ In the same way, the thermal decarboxylation of the $\alpha\gamma$ -diaceto- β -(2-methoxy-5-methyl-phenyl)-glutaconic anhydride, m.p. 168°C, produced a lactone, m.p. 164°C, which with caustic alkalis gave the hydroxy-diphenyl, m.p. 85°C, and the hydroxy-diphenyl carboxylic acid, m.p. 213°C, and not the other isomeric acid, m.p. 192°C. Hence the acid, m.p. 213°C, is a para-hydroxy acid and the other with m.p. 192°C, the ortho-hydroxy acid, and not vice versa as given before.⁵ (1. c. p. 210-11).



As remarked before (part IV, p. 221 ; Part V, p. 211) in view of the fact that Einhorn's method is known to favour o-acetylation, the α -C-acylation of β -aryl-glutaconic anhydrides and especially the further γ -C-acylation of α -C-acyl-glutaconic anhydrides to give $\alpha\gamma$ -C-diacyl- β -aryl-glutaconic anhydrides by Einhorn's method seems unusual if the acidity and colouration with ferric chloride of all these compounds are due to the hydroxy group arising out of the wandering of the mobile hydrogen atom in the glutaconic anhydride to the neighbouring carbonyl group. This question could be now settled by further

acylating the α -C-acyl-glutaconic anhydride in the γ -position with a different acid chloride and comparing this $\alpha\gamma$ -C-diacyl-glutaconic anhydride with the one obtained by reversing the sequence of the acid chlorides employed. If the glutaconic anhydride had the unsymmetrical hydroxy-anhydride structure (XV) these two $\alpha\gamma$ -C-diacyl-anhydrides, *e.g.*, (XVI) and (XVIII) would be different. In the C-arylation of β -aryl-glutaconic



anhydrides by Einhorn's method, we have a reaction wherein the attachment of the aryl group to the α -carbon atom in the glutaconic anhydride can be definitely proved as shown before in the case of C-benzoylation. Among the various other aromatic acid chlorides tried, only *p*-bromo-benzoyl chloride was found to react with β -4-methoxy-phenyl-glutaconic anhydride, and the resulting α -*p*-bromo-benzoyl- β -4-methoxyphenyl-glutaconic anhydride, m.p. 146°C (XVII) gave a ketonic acid, m.p. 123°C (II) and a lactone, m.p. 208°C (III). It gets decomposed into the β -4-methoxyphenyl glutaconic acid and *p*-bromo-benzoic acid in a way similar to the α -benzoyl-glutaconic anhydride (I). Now this α -benzoyl-glutaconic anhydride on further *p*-bromo-benzoylation by Einhorn's method gave the α -benzoyl- γ -*p*-bromo-benzoyl-glutaconic anhydride, m.p. 164°C (XVI). Similarly the α -*p*-bromo-benzoyl-glutaconic anhydride (XVII) on further benzoylation gave the α -*p*-bromo-benzoyl- γ -benzoyl-glutaconic anhydride (XVIII) and this compound has been found to be identical with (XVI). Hence we are forced to the conclusion that not only the glutaconic anhydride cannot have the unsymmetrical hydroxy anhydride structure (XV) but that it must be represented by a symmetrical constitution (XIX), in other words the α - and γ - positions in β -aryl-glutaconic anhydrides are identical and the mobile hydrogen atom, which is responsible for the acidity and ferric chloride colouration,

constantly wanders between these two positions. This, thus, is an extension of the constitution suggested by Thorpe and co-workers⁹ to account for the identity of the α - and γ - positions in the case of glutaconic acids and esters, to the glutaconic anhydrides.

The C-acetylation and C-benzoylation of β -aryl glutaconic anhydrides in which the α -position is already substituted by an alkyl group, would prove interesting as it is expected to throw more light on the question of the tautomerism of β -aryl-glutaconic anhydrides. The alkylation of β -aryl-glutaconic esters in the α -position is at present being attempted by Thorpe and Wood's method.¹⁰

EXPERIMENTAL

C-Benzoylation of β -4-methoxyphenyl-glutaconic anhydride: Formation of α -benzoyl- β -4-methoxyphenyl-glutaconic anhydride (I).—The glutaconic anhydride (10 g.) was dissolved in warm pyridine (30 c. c.), the solution cooled in ice-water and benzoyl chloride (2.5 c.c.) was added drop by drop with stirring and shaking the reaction mixture continuously. The dark green pasty reaction mixture, was kept at room temperature for 15 minutes, then dissolved in water and acidified by hydrochloric acid (30 c.c.). The red resinous mass which separated was dissolved in cold sodium carbonate solution, the solution treated with animal charcoal, then washed with ethyl acetate, ether and acidified. The resulting oily mass which solidified by rubbing with cold water, was filtered, washed with small amount of ice-cold methyl alcohol and dried. Yield 7.3 g. This was dissolved in hot benzene, filtered and the filtrate concentrated to 20 c.c. by distilling off the benzene under reduced pressure. The unchanged glutaconic anhydride which separated on cooling was filtered and the filtrate diluted with petrol-ether when the α -C-benzoyl-anhydride separated in yellow prisms. It was rapidly crystallised from methyl alcohol in elongated parallelogramic plates, m.p. 119°C (decomp.). Yield 4.5 g. (Found : C = 70.5% ; H = 4.2% ; $C_{15}H_{14}O_5$ requires C = 70.8% ; H = 4.3%). The compound gives a dark green colouration with alcoholic ferric chloride and an insoluble sodium salt even with 5% alkalis. The compound could be decomposed into benzoic acid and β -4-methoxy-phenyl-glutaconic acid by refluxing with

9. Thorpe, J.C.S., 1905, 87, 1680 ;

Thole and Thorpe, J.C.S., 1911, 99, 2193.

10. Thorpe and Wood, J.C.S., 1913, 103, 1752.

absolute alcohol for 3 hours, distilling off the alcohol and refluxing the residue with 10% sodium hydroxide for 15 minutes. The alkali solution was filtered, washed with ether and acidified. The mixed acids were separated by ether in which the glutaconic acid is insoluble.

The 2-p-methoxyphenyl-3-benzoyl-propylene-1-carboxylic acid (II).—The above α -C-benzoyl-anhydride (5 g.) was intimately mixed with normal sodium hydroxide solution (75 c.c.) warmed on a waterbath for 10 minutes and the resulting clear solution kept overnight at room temperature and acidified. The resulting ketonic acid was dissolved in cold sodium carbonate solution, washed with ether, precipitated by acids and crystallised from methyl alcohol in silky needles, m.p. 114°C (decomp.) (Found : C=72.8% ; H=5.4% ; Eq.=290 ; $\text{C}_{18}\text{H}_{16}\text{O}_4$ requires C=73.0% ; H=5.4% ; Eq.=296). Semicarbazone crystallised from alcohol, m.p. 162°C (decomp.). This ketonic acid on thermal decarboxylation produced a ketonic oil which gave a semicarbazone, m.p. 142°C (decomp.).

The lactone (III) of the above ketonic acid was obtained by refluxing with hydrochloric acid for $\frac{1}{2}$ hour or by dissolving in conc. sulphuric acid, keeping at room temperature for 2 hours and pouring in water. The lactone also resulted on refluxing the α -C-benzoyl anhydride with hydrochloric acid. The product was filtered washed with hot sodium carbonate solution, water and crystallised from methyl alcohol in hexagonal light plates, m.p. 145°C . Yield quantitative. (Found : C=77.3% ; H=5.0% ; $\text{C}_{18}\text{H}_{14}\text{O}_3$ requires C=77.7% ; H=5.0%).

Formation of the lactone, m.p. 145°C , by the decomposition of the α -benzoyl anhydride, m.p. 119°C .—The α -benzoyl anhydride was decomposed at $120^{\circ}\text{C}/50$ mm., and after the carbon-dioxide evolution stopped, the residual violet contents which solidified on cooling were rubbed with hot methyl alcohol, and the precipitated lactone purified as above ; mixed m.p. 145°C . *Reconversion of the lactone 145°C , into the ketonic acid m.p. 114°C .*—The lactone (1 g.) was dissolved in boiling alcohol, sodium hydroxide (2 g.) in a little water added, the solution warmed on a water bath for a few minutes and the alcohol evaporated at room temperature. Water was added to the residue, any unchanged lactone filtered out, the solution washed with ether, and the ketonic acid m.p. 114°C precipitated by acids.

γ -C-Benzoylation of α -C-benzoyl- β -4-methoxyphenyl-glutaconic anhydride : Formation of $\alpha\gamma$ -dibenzoyl- β -4-methoxyphenyl-glutaconic anhydride (VI).—The α -benzoyl anhydride, m.p.

119°C, was dissolved in pyridine by warming and the requisite amount of benzoyl chloride added gradually with shaking. The reaction mixture was heated on a water-bath for a few minutes then dissolved in water and acidified by hydrochloric acid. The resinous mass which separated was dissolved in cold sodium carbonate solution, filtered and acidified. The resulting product was rubbed with methyl alcohol and the granular dibenzoyl anhydride thus separated was crystallised from ethyl acetate in hexagonal plates, m.p. 194°C (decomp.). (Found: C=72.8%; H=4.0%. $C_{26}H_{18}O_6$ requires C=73.2%; H=4.2%). The compound gave blue colouration with alcoholic ferric chloride, and an insoluble sodium salt with dilute alkalis. The compound is remarkably stable towards boiling water, alcohol or hydrochloric acid.

$\alpha\gamma$ -Dibenzoyl- β -4-methoxyphenyl-propylene (VII) was obtained by warming the $\alpha\gamma$ -dibenzoyl anhydride (1 g.) with normal sodium hydroxide solution, till the colour of the solution changed to faint yellow and an oily product began to separate. It was kept overnight at room temperature and the resulting diketone was filtered, washed with water and crystallised from alcohol in silky needles, m.p. 124°C; Yield 0.7 g. (Found: C=80.4%; H=5.2%. $C_{24}H_{20}O_3$ requires C=80.9%; H=5.6%). The semicarbazone, m.p. 172°C (decomp.).

Thermal decarboxylation of $\alpha\gamma$ -dibenzoyl anhydride, m.p. 194°C.—The dibenzoyl anhydride was decomposed at 200°C/40 mm.; the residue treated with boiling methyl alcohol and the insoluble solid was filtered, washed with boiling sodium carbonate solution, water, dried and crystallised from benzene in rectangular rods, m.p. 193°C. (Found: C=78.1%; H=4.5%. $C_{25}H_{18}O_4$ requires, C=78.5%; H=4.7%). The compound is not acted upon even by boiling alkalis. It is however hydrolysed by alcoholic alkalis thus: the compound (1 g.) in suspension in boiling methyl alcohol was mixed with sodium hydroxide (2 g.) in a little water, when suddenly the solution turned deep orange and the substance disappeared. The solution was filtered, methyl alcohol removed at room temperature, water added and the whole kept overnight, when the above diketone, m.p. 124°C, was obtained.

The α -benzoyl- β -(2-methoxy-5-methylphenyl)-glutaconic anhydride was obtained by treating a solution of the β -(2-methoxy-5-methylphenyl)-glutaconic anhydride in pyridine with the requisite quantity of benzoyl chloride gradually at the room temperature. The reaction mixture was dissolved in water and

acidified with hydrochloric acid. The compound was isolated by a method identical with the one followed in the case of the α -benzoyl anhydride, m.p. 119°C (I). It was washed with cold methyl alcohol, dried, and crystallised from ethyl acetate and then from alcohol in yellow needles, m.p. 158°C (decomp.). (Found: C=71.2%; H=4.6%. $\text{C}_{20}\text{H}_{16}\text{O}_5$ requires C=71.4%; H=4.7%). The compound gives a blue colouration with alcoholic ferric chloride. On heating its alkaline solution on a water-bath, an oily acid was obtained, which distilled with decomposition, and hence could not be purified. However, by the action of hydrochloric acid or sulphuric acid, this ketonic acid gave a lactone which crystallised from methyl alcohol in colourless parallelogramic plates, m.p. 126°C . This lactone is also obtained from the α -benzoyl anhydride, m.p. 158°C by refluxing with hydrochloric acid or by thermal decarboxylation. (Found: C=77.8%; H=5.4%. $\text{C}_{19}\text{H}_{16}\text{O}_3$ requires C=78.1%; H=5.5%).

Thermal decarboxylation of the $\alpha\gamma$ -diaceto- β -4-methoxy-phenyl glutaconic anhydride⁵ (X).—The $\alpha\gamma$ diacetyl anhydride m.p. 108°C (4 g.) was decomposed at $150\text{--}160^{\circ}\text{C}/5\text{ mm.}$ till the carbon dioxide evolution ceased, the residue dissolved in boiling alcohol, the solution refluxed with animal charcoal, filtered and precipitated by water. The substance which separated after keeping overnight was filtered, washed with boiling sodium carbonate solution, water, and finally crystallised from dilute methyl alcohol in parallelogramic plates, m.p. 111°C (XI), yield 1 g. (Found: C=69.6%; H=5.4%. $\text{C}_{15}\text{H}_{14}\text{O}_4$ requires C=69.7%; H=5.4%). By the action of boiling 10% sodium hydroxide solution, this decarboxylation product slowly dissolved and was transformed into the phenol-3-methoxy-4'-methyl-2'-hydroxy-diphenyl—m.p. 118°C^4 , and the phenolic carboxylic acid, m.p. 132°C , which now must be the 3-methoxy-4'-methyl-2'-hydroxy-diphenyl-5'-carboxylic acid.

Thermal decarboxylation of $\alpha\gamma$ -diaceto- β -(2-methoxy-5-methyl-phenyl)-glutaconic anhydride⁵.—The C-diacetyl anhydride, m.p. 168°C (5g.) was decomposed at $180^{\circ}\text{C}/40\text{ mm.}$, the residue dissolved in boiling methyl alcohol, the solvent evaporated and the residue washed with boiling sodium carbonate, water and extracted with 75% methyl alcohol. The exact was diluted with water and kept overnight, and the compound thus separated was filtered and crystallised from methyl alcohol in fine yellow needles, m.p. 164°C , yield 1.5g. (Found: C=70.5%; H=5.8%. $\text{C}_{16}\text{H}_{16}\text{O}_4$ requires C=70.6%; H=5.9%). By refluxing with

10% sodium hydroxide solution, this compound is transformed into the phenol-1-methoxy-4:4'-dimethyl-2'-hydroxy-diphenyl, m.p. 85°C, and the phenolic acid m.p. 213°C. (decomp.) which now must be 1-methoxy-4:4'-dimethyl-2'-hydroxy-diphenyl-5'-carboxylic acid.

p-Bromo-benzoylation of β -4-methoxy-phenyl-glutaconic anhydride: Formation of α -*p*-bromobenzoyl- β -4-methoxy-phenyl-glutaconic anhydride (XVII).—The glutaconic anhydride (5.5g.) was dissolved in warm pyridine (25c.c.), the solution cooled in ice and finely powdered *p*-bromo-benzoyl chloride (5.7g.) was added in small portions, stirring the reaction mixture all the time. After keeping in ice bath for 15 minutes and then at room temperature, the green semi-solid reaction mixture was mixed with water (200c.c.) and acidified with hydrochloric acid (25c.c.). The resulting granular precipitate was dissolved in cold dilute sodium carbonate solution, filtered, washed with ether and reprecipitated by acids; yield 7.5g. This was treated with boiling benzene (50c.c.), the insoluble *p*-bromobenzoic acid—2g.—and the unchanged glutaconic anhydride—1g.—which separated on cooling and scratching the benzene filtrates were filtered out, the filtrates concentrated to 10c.c. by distilling off the benzene under reduced pressure, and precipitated by petrol ether. The α -*p*-bromobenzoyl-anhydride which separated on scratching and keeping was filtered, washed with cold methyl alcohol and dried. It was dissolved in excess of cold benzene, some more unchanged glutaconic anhydride filtered out, the filtrates concentrated under reduced pressure and precipitated by petrol ether when the compound separated in yellow microscopic needles, m.p. 145°C (decomp.). It was rapidly recrystallised from methyl alcohol. (Found: C=56.5%; H=3.1%; Br=19.8%. $C_{19}H_{13}O_5Br$ requires C=56.8%; H=3.2%; Br=20.0%). The compound gives a violet colouration with alcoholic ferric chloride and an insoluble sodium salt with dilute alkalis. The compound gets decomposed into *p*-bromo-benzoic acid and β -4-methoxyphenyl-glutaconic acid, by refluxing with absolute alcohol, distilling off the alcohol and refluxing the residue with 10% sodium hydroxide solution until the insoluble solid dissolved. The alkali solution was filtered, washed with ether and acidified, and the acids were separated by treating with boiling water in which the *p*-bromobenzoic acid is insoluble.

The 2-*p*-methoxyphenyl-3-*p*-bromobenzoyl-propylene-1-carboxylic acid (as II).—This ketonic acid was obtained by

warming the above α -*p*-bromobenzoyl anhydride with 5% sodium hydroxide solution, keeping the alkali solution overnight and acidifying. It crystallised from methyl alcohol in colourless flat needles, m.p. 123° (decomp.). (Found: C=57.3%; H=4.0%; Br=21.0%. $C_{18}H_{15}O_4Br$ requires C=57.6%; H=4.0%; Br=21.3%). Semicarbazone m.p. 174°C (decomp.). By heating or by hot alkali, the ketonic acid lost carbon dioxide and produced a ketone which crystallised from alcohol in elongated hexagonal plates, m.p. 115°C. (Found: C=61.4%; H=4.3%. $C_{17}H_{15}O_2Br$ requires C=61.6%; H=4.5%). Semicarbazone m.p. 192°C (decomp.).

The Lactone like (III) was obtained by decomposing the above α -*p*-bromobenzoyl anhydride (1 g.) at 150-160°C/150 mm. and rubbing the violet residue with hot methyl alcohol. The insoluble lactone was washed with boiling sodium carbonate solution, water and crystallised from acetone (animal charcoal) in colourless light needles, m.p. 208°C; yield 0.7 g. (Found: C=61.3%; H=3.5%; Br=22.1%. $C_{18}H_{15}O_3Br$ requires C=60.5%; H=3.6; Br=22.4%). This lactone could also be obtained by refluxing the α -*p*-bromobenzoyl anhydride with hydrochloric acid, or by refluxing the ketonic acid m.p. 123°C with absolute alcoholic hydrochloric acid. By refluxing with 5% alcoholic sodium hydroxide for 15 minutes and removing the alcohol at room temperature, this lactone produces the above ketone, m.p. 115°C and a small amount of the ketonic acid, m.p. 123°C.

*γ -C-Benzoylation of α -*p*-bromobenzoyl- β -4-methoxyphenyl-glutaconic anhydride: Formation of α -*p*-bromobenzoyl- γ -benzoyl- β -4-methoxyphenyl-glutaconic anhydride (XVIII).*—The α -*p*-bromobenzoyl anhydride, m.p. 145°C (1 g.) was dissolved in warm pyridine (10 c.c.), benzoyl chloride (0.7 g.) was gradually added with shaking and the reaction finished by warming on a water-bath for 20 minutes. The reaction mixture was poured in water, acidified with hydrochloric acid (10 c.c.) the resinous precipitate was dissolved in cold alcohol, diluted with water and acidified. The sticky precipitate which solidified on decanting off the aqueous portion and rubbing with water, was washed with boiling methyl alcohol and crystallised by dissolving in hot benzene and precipitating with petrol-ether. This was again washed with cold methyl alcohol and crystallised as above in microscopic needles, m.p. 164°C (decomp.). This compound gave red colouration with alcoholic ferric chloride, and its sodium salt is insoluble in dilute alkalis. (Found: C=61.4%; H=3.3%;

Br=15.3%. $C_{26}H_{17}O_6Br$ requires C=61.8%; H=3.5%; Br=15.8%).

*γ -p-Bromobenzoylation of α -benzoyl- β -4-methoxyphenyl glutaconic anhydride. Formation of α -benzoyl- γ -p-bromobenzoyl- β -4-methoxyphenyl-glutaconic anhydride (XVI).—*The α -benzoyl-glutaconic anhydride is dissolved in warm pyridine and is treated with powdered *p*-bromobenzoyl chloride in small portions. The reaction is completed by heating on a water-bath, and the α -benzoyl- γ -p-bromobenzoyl glutaconic anhydride is isolated just as above. It melts at 164°C (decomp.) and is identical with the α -p-bromobenzoyl- γ -benzoyl glutaconic anhydride described above.

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METHOXY TOLYL SUCCINIC ACIDS

By

V. A. VYAS, K. V. BOKIL AND K. S. NARGUND

DAVE and Nargund reported the preparation of isomeric hydroxy and methoxy phenyl succinic acids. (Jour. Bom. Univ., 1938, Vol. 7, part 3, page 196). Methoxy tolyl succinic acids which were required in connection with the work on synthetical anthelmintics (see the following paper) are now described in the present communication. The mode of preparation of these succinic acids was that of Lapworth and collaborators. (J. C. S., 1922, 49, 1699, 2741, *ibid.*, 1925, 560). The method consists in treating an appropriate aldehyde with a solution of sodium cyanoacetate when a substituted acrylic acid is obtained. This, on esterification, gives an ethyl ester. Addition of hydrogen cyanide to this ester, followed by hydrolysis of the resulting dicyano compound gives the desired succinic acid. The use of 25 per cent. hydrochloric acid has been found to be better than concentrated hydrochloric acid in the hydrolysis of the dicyano compounds.

EXPERIMENTAL

Sodium cyanoacetate solution was prepared as described in organic syntheses, vol. 7, page 20. The other steps in the syntheses were as described in organic syntheses, vol. 8, page 88. Methoxy tolyl aldehydes were prepared by Adam's modification of Gattermann's method. The compounds are described in tabular forms for the sake of brevity :—

Name of the compound	Formula	Properties	Analysis	
			Found	Required for
<i>α</i> -Cyano-β-(4-methoxy-3-tolyl)-acrylic acid.	C ₁₂ H ₁₁ O ₃ N.	Wooly needles from acetic acid m.p. 217°.	Eqt. Wt. 214	217
Methyl-α-cyano-β-(4-methoxy-3-tolyl)-acrylate.	C ₁₃ H ₁₃ O ₃ N.	Fine long silky needles from either alcohol or dilute acetic acid m.p. 153-154°.	C, 67.4 H, 5.8	C, 67.5 H, 5.6
Ethyl-α-cyano-β-(4-methoxy-3-tolyl)-acrylate.	C ₁₄ H ₁₅ O ₃ N.	Short needles from alcohol m.p. 117°.	C, 68.7 H, 6.4	C, 68.8 H, 6.1
4-Methoxy-3-tolyl succinic acid.	C ₁₂ H ₁₄ O ₄	Crystallised from water or acetic acid in plates m.p. 192°.	C, 60.7 H, 5.7 Eq. Wt. 115.2	C, 60 H, 5.9 Eq. Wt. 119
Methyl-(4-methoxy-3-tolyl)-succinate.	C ₁₄ H ₁₆ O ₆	Short wooly needles from dilute methyl alcohol m.p. 75°.	C, 62.9 H, 6.9	C, 63.1 H, 6.8
Ethyl-(4-methoxy-3-tolyl) succinate.	C ₁₆ H ₁₈ O ₆	Colourless liquid b.p. 175-180° at 8 mm. D ₄ ^{38.5} = 1.087. N _D ^{38.5} = 1.49334.	C, 65.2 H, 7.2	C, 65.3 H, 7.5
4-methoxy-3-tolyl succinic anhydride.	C ₁₂ H ₁₂ O ₄	Prepared from the acid by heating with acetyl chloride. Thin shining plates from petroleum ether m.p. 80°.	C, 65.2 H, 5.8	C, 65.5 H, 5.5

Name of the compound	Formula	Properties	Analysis	
			Found	Required for
<i>Mono anilide of 4-methoxy-3-tolyl succinic acid.</i>	$C_{18}H_{19}O_4N$	Prepared by the action of equivalent quantity of aniline on anhydride Star shaped crystals from alcohol m.p. 168°.	Eqt. wt. 317.0	313
<i>Mono-p-toluidide of 4-methoxy-3-tolyl succinic acid.</i>	$C_{19}H_{21}O_4N$	Needles from alcohol m.p. 127°.	Eqt. wt. 324.9	327
<i>α-cyano-β-(4-methoxy-2-tolyl)-acrylic acid.</i>	$C_{13}H_{11}O_3N$	Long pale yellow rods from either alcohol or acetic acid m.p. 225°.	Eqt. wt. 217.4	217
<i>Methyl α-cyano-β-(4-methoxy-2-tolyl)-acrylate.</i>	$C_{13}H_{13}O_3N$	Yellowish long needles from alcohol m.p. 118°.	C, 67.3 H, 5.7	C, 67.5 H, 5.6
<i>Ethyl α-cyano-β-(4-methoxy-2-tolyl)-acrylate.</i>	$C_{14}H_{15}O_3N$	Yellow needles from alcohol m.p. 93-94°.	C, 68.4 H, 6.2	C, 68.6 H, 6.1
<i>4-methoxy-2-tolyl succinic acid.</i>	$C_{12}H_{14}O_5$	Crystallised from ethyl acetate and petroleum ether or boiling water m.p. 196°.	Eqt. wt. 120.0 C, 60.3 H, 6.0	119 C, 60.5 H, 5.9
<i>Methyl (4-methoxy-2-tolyl)-succinate.</i>	$C_{14}H_{16}O_5$	Colourless liquid b. p. 160° at 5 mm. $D_4^{25} = 1.095, N_D^{25} = 1.49429$.	C, 62.9 H, 6.7	C, 63.2 H, 6.8

<i>Ethyl-4-methoxy-2-tolyl-succinate</i>	$C_{16}H_{22}O_6$	Colourless liquid b.p. 165° at 5 mm. $D_4^{37.5} = 1.1460$, $N_D^{37.5} = 1.50598$.	C, 70.8 H, 7.5	C, 70.9 H, 7.3
<i>4-methoxy-2-tolyl succinic anhydride.</i>	$C_{13}H_{12}O_4$	Prepared from the acid and acetyl chloride a thick yellowish liquid b. p $205^{\circ}-210^{\circ}$ at 8 mm.	C, 65.4 H, 8.5	C, 65.5 H, 8.5
<i>Mono anilide of 4-methoxy-2-tolyl succinic acid.</i>	$C_{18}H_{19}O_4N$	Fine needles from alcohol m.p. 156° .	Eqt. Wt. 315.0	317
<i>Mono p-toluide of 4-methoxy-2-tolyl succinic acid.</i>	$C_{19}H_{21}O_4N$	Colourless needles from alcohol m.p. 162° .	Eqt. Wt. 324.2	329
<i>α-cyano β-(6-methoxy-3 tollyl)-acrylic acid.</i>	$C_{12}H_{11}O_3N$	Short thick yellow needles from acetic acid m.p. 228° .	Eqt. Wt. 211.0	217
<i>Methyl α-(cyano-β 6-methoxy-3-tolyl)-acrylate.</i>	$C_{13}H_{15}O_3N$	Yellow thin plates from methyl alcohol m.p. $13\frac{1}{2}^{\circ}$.	C, 67.2 H, 5.6	C, 67.5 H, 5.6
<i>Ethyl α-(cyano-β 6-methoxy-3-tolyl) acrylate.</i>	$C_{14}H_{17}O_3N$	Thin long needles from methyl alcohol m.p. 83° .	C, 68.3 H, 6.4	C, 68.6 H, 6.1
<i>6-methoxy-3-tolyl succinic acid</i>	$C_{13}H_{14}O_5$	Thin flat blades from hot water m.p. 186° .	C, 60.4 H, 6.1 Eq. Wt. 120.5	C, 60.5 H, 5.9 119

Name of the compound	Formula	Properties	analysis	
			Found	Required for
<i>6-methoxy-3-tolyl succinic anhydride.</i>	$C_{12}H_{12}O_4$	Prepared by boiling the acid with acetic anhydride. Long rectangular plates from petroleum ether m.p. 119°.	C, 65.7 H, 5.4	C, 65.5 H, 5.4
<i>Mono anilide of 6-methoxy-3-tolyl succinic acid.</i>	$C_{18}H_{19}O_4N$	Colourless needles from alcohol m.p. 154°.	Eqt. wt. 310	313
<i>Mono p-toluidide of 6-methoxy-3-tolyl succinic acid.</i>	$C_{18}H_{21}O_4$	Colourless short wooly needles from alcohol m.p. 197°.	Eqt. wt. 326.1	327

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SYNTHETICAL ANTHELMINTICS PART I

α -SUBSTITUTED- γ -BUTYROLACTONES

By

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ANTHELMINTICS (anti = against and helminthos = worms) are substances which are used to bring about the death or expulsion of worms parasitic in men and animals. Usually, however, the term anthelmintic is applied to drugs capable of killing or expelling worms in the intestine. The damages wrought by these intestinal worms are many. (i) They may use up the food of the host thus starving the host. This damage is usually not of importance except in case of large and numerous tape worms. (ii) They may cause mechanical injury to the intestine; for example hook worms bite the intestinal wall. (iii) They may produce toxic substances which may have a serious effect on the blood and the nervous systems of the host. Thus it will be seen that an ideal anthelmintic by removing these worms would be a great boon to mankind.

The question of the relationship between the chemical constitution and the anthelmintic action is not quite clear. In certain types of anthelmintics it is considered that a lactone group is essential to develop the anthelmintic properties in the substance. (Trendelenburg, Arch. F. Exp. Path. und Pharm., 1916, 79). Lautenschlager (Ber. Deutsch. Pharmaz. Ges., 1921, 279.) has shown that purely aliphatic lactones, like butyrolactone or paraconic acid lactone have no anthelmintic action. But lactones attached to a benzene nucleus, like phenyl-paraconic acid lactone, have marked anthelmintic properties. Rosenmond and Schapiro (Arch. Pharm., 1934, 271, 315) prepared a number of γ -butyrolactones with methoxy-phenyl or hydroxy-phenyl or methoxy-tolyl group as substituent on γ -carbon atom. Some of these lactones had very remarkable anthelmintic properties. The broad conclusions to be drawn from their results are :—

- (i) A butyrolactone structure is essential for the development of anthelmintic properties.

- (ii) The lactone must be attached to a benzene nucleus with hydroxy or methoxy group as a substituent.

With a view to extending the work of Rosenmund and Schapiro (loc. cit.) we have now prepared lactones with methoxy-phenyl or methoxy-tolyl groups as substituents on the α -carbon atom.

The method selected for the preparation of such lactones was the reduction of an acid ester of substituted succinic acid. It has been shown that the acid ester obtained by the action of alcohol on a substituted succinic anhydride has the carboxyl group attached to the carbon carrying the substituent. (Bone, Sudborough and Sprankling J. C. S. 1904, 534; Wegscheider and Hecht Mon. 1903, 24, 413-433; Anschütz and coworkers A, 354, 117-150).

Phenyl succinic anhydride on boiling with absolute alcohol gave α -phenyl- β -carbethoxy propionic acid which on reduction with sodium and alcohol gave α -phenyl- γ -butyrolactone identical with the lactone described by Carre and Libermann (Comp. Ren. 1903, 196, 117) who prepared it by treatment of the sodio derivative of benzyl cyanide with chlorhydrin and subsequent hydrolysis. α -p-methoxy-phenyl- β -carbethoxy propionic acid on reduction gave α -p-methoxy-phenyl- γ -butyrolactone identical with the lactone synthesised from p-methoxy-benzyl cyanide following the method of Carre and Libermann (loc. cit.). Similarly α -o-methoxy-phenyl-butyrolactone was prepared by both the methods. α -4-methoxy-3-tolyl- γ -butyrolactone and α -6-methoxy-3-tolyl- γ -butyrolactone have been prepared by the reduction of the acid esters. No synthesis of these lactones could be effected as the corresponding substituted benzyl cyanides are unknown.

EXPERIMENTAL

α -phenyl- γ -butyrolactone.— *α -phenyl- β -carbethoxy propionic acid* was prepared by boiling phenyl succinic anhydride with an equivalent quantity of absolute alcohol on water bath. It was purified by recrystallisation from benzene and obtained in small plates from benzene m.p. 96° . (Found: Eqt. wt. 219.9. $C_{12}H_{14}O_4$ requires eqt. wt. 223). The above ester (25 gms.) dissolved in absolute alcohol was added as rapidly as possible to molten sodium (14 gms) kept in a three-necked flask with a reflux condenser and stirrer and heated in an oil bath at 100° . More alcohol (90 cc) was added and heating continued till the temperature of the bath was 140° , and the whole of the sodium dissolved. It was cooled and water (50 cc) added and heated

on water bath for half an hour. Alcohol was removed and then acidified with sulphuric acid and warmed. It was then extracted with ether and ether removed without drying. The recovered substance was left overnight with excess of sodium bicarbonate. The lactone was then extracted with ether, dried, ether removed and the residue distilled under reduced pressure. α -phenyl- γ -butyrolactone had b.p. 170–172 at 10 mm $D_4^{28}=1.1507$ and $n_D^{28}=1.53432$. Carre and Libermann (loc. cit.) give the boiling point of this lactone as 203°–205° at 30 mm. The same lactone was prepared by Carre and Libermann's method and had identical properties. The lactone on dissolving in warm sodium hydroxide and then acidifying in cold with slight excess of sulphuric acid gave α -phenyl- γ -hydroxy butyric acid m.p. 106°. Carre and Libermann give the m.p. of this acid as 99–100°.

α -p-methoxy-phenyl- γ -butyrolactone.— *α -p-methoxy-phenyl- β -carbethoxy propionic acid* was prepared by boiling together p-methoxy-phenyl succinic anhydride and absolute alcohol. It was soluble in alcohol, chloroform, and acetic acid and sparingly soluble in ethyl acetate and petroleum ether. It crystallised from petroleum ether in square plates, m.p. 83°. (Found : Eqt. wt. 251.8. $C_{15}H_{16}O_5$ requires eqt. wt. 252). Reduction with sodium and alcohol and working it up as described before gave *α -p-methoxy-phenyl- γ -butyrolactone* b.p. 215°–220° at 25 mm. It had $D_4^{35}=1.0736$ and $n_D^{35}=1.54335$. (Found : Eqt. wt. by back titration, 187. C, 68.6. H, 6.5 per cent. $C_{11}H_{12}O_3$ requires eqt. wt. 192, C, 68.7. H, 6.3 per cent.). *Synthesis of the above lactone:*—p-methoxy-benzyl cyanide (Pschorr, Wolfes and Buckow B. 33,171) (15 gms) sodamide (7 gms) and dry ether (100 cc) were warmed till the reaction was complete. Chlorhydrin (8 gms) was then added in small amounts. It was then heated on water bath for two hours. It was decomposed with ice and hydrochloric acid, extracted with ether dried and ether removed. The residue distilled under reduced pressure. *β -p-methoxy-phenyl- β -cyano propyl alcohol* had b.p. 135°–140° at 10 mm. (Found : N, 7.5 per cent. $C_{11}H_{13}O_2N$ requires N, 7.3 per cent.). The above cyano-compound was hydrolysed with excess of 20 per cent. sodium hydroxide solution and then acidified and warmed. It was extracted with ether. The residue left after removing ether was purified by sodiumbicarbonate solution. The lactone obtained had b.p. 210° at 12 mm. and had the same properties as described in case of *α -p-methoxy-phenyl- γ -butyrolactone.*

The above lactone on dissolving in hot alkali and neutralisation in cold gave α -p-methoxy-phenyl- γ -hydroxy butyric acid m.p. 88-89°, star shaped needles from benzene. It was easily converted into lactone when kept at room temperature for some days or in a few minutes at 60°. (Found: Eqt. wt. 208; C, 62.8; H, 6.9 per cent. $C_{11}H_{14}O_4$ requires eqt. wt. 210; C, 62.9; H, 6.7 per cent.).

α -o-methoxy-phenyl- γ -butyrolactone.— *α -o-methoxy-phenyl- β -carbethoxy propionic acid* was prepared by boiling together o-methoxy-phenyl succinic anhydride (Dave and Nargund, Jour. Bom. Univ., 1938, Vol. 7, Part 3, page 196) with a large excess of absolute alcohol. It was a syrupy liquid. (Found: Eqt. wt. 254. $C_{13}H_{16}O_5$ requires eqt. wt. 252). On reduction, 29 gms of above ester gave 13 gms of α -o-methoxy-phenyl- γ -butyrolactone b.p. 185°-190° at 17 mm. It had $D_4^{35}=1.0791$ and $n_D^{35}=1.34157$. (Found: Eqt. wt. by back titration, 185.5 C, 68.7; H, 6.4 per cent. $C_{11}H_{12}O_3$ requires Eqt. wt. 192. C, 68.7 H, 6.3 per cent.).

Synthesis of the above lactone by Carre and Libermann's method.—o-methoxy-benzyl-cyanide (Lauer and Hansen, J. A. C. S., 1939, 61, 3040), (22 gms) sodamide (6 gms), dry ether (100 cc) and chlorohydrin (13 gms), when worked up as described previously, gave *β -o-methoxy-phenyl- β -cyano propyl alcohol*, b.p. 127°-129° at 8 mm. (Found: N, 7.8 per cent. $C_{11}H_{15}O_2N$ requires N, 7.3 per cent.). On hydrolysis with ten per cent. alkali followed by acidification and warming gave 6 gms of α -o-methoxy-phenyl- γ -butyrolactone with properties identical with those of the lactone obtained by the reduction of the acid ester.

α -o-methoxy-phenyl- γ -hydroxy butyric acid could not be obtained from the above lactone on account of the ease with which it passed into the lactone.

α -4-methoxy-3-tolyl butyrolactone.— *α -4-methoxy-3-tolyl- β -carbethoxy propionic acid* was obtained from 4-methoxy-3-tolyl succinic anhydride (Vyas, Bokil and Nargund, preceding paper) and absolute alcohol. It was a low melting solid crystallising from methyl alcohol in minute needles, m. p. 42°. (Found: Eqt. wt. 262. $C_{14}H_{18}O_5$ requires eqt. wt. 266). The above compound (15 gms) on reduction with sodium and alcohol gave 3.8 gms of *α -4-methoxy-3-tolyl- γ -butyrolactone* b.p. 200°-210°

at 4 mm. $D_4^{88} = 1.1888$ and $n_D^{88} = 1.53880$. (Found : C, 69.8; H, 7.1; $C_{12}H_{14}O_8$ requires C, 69.9; H, 6.8 per cent.). α -4-methoxy-3-tolyl- γ -hydroxy butyric acid could not be prepared in pure condition.

α -6-methoxy-3-tolyl- γ -butyrolactone.— *α -6-methoxy-3-tolyl- β -citrithoxy propionic acid* was prepared from 6-methoxy-3-tolyl succinic anhydride (Vyas, Bokil and Nargund, this vol., preceding paper) and absolute alcohol. It was soluble in benzene, chloroform and alcohol. It crystallised from benzene in needles, m.p. 102° . (Found : Eqt. wt. 260.8. $C_{14}H_{18}O_5$ requires eqt. wt. 266). The above compound (10 gms) on reduction gave 2.2 gms of *α -6-methoxy-3-tolyl- β -butyrolactone* b.p. $195-200$ at 12 mm.; it solidified after some time, was soluble in the usual solvents and crystallised from benzene-petrol mixture in needles m.p. 62° . (Found : Eqt. wt. 206.1; C, 69.6; H, 6.9. $C_{12}H_{14}O_3$ requires eqt. wt. 206. C, 69.9 H, 6.8 per cent.).

α -6-methoxy-3-tolyl- γ -hydroxy butyric acid prepared from the above lactone was soluble in alcohol, acetic acid, ethyl acetate and hot water. It crystallised from hot water or benzene, m.p. 124° . When crystallised from benzene it had a low m.p., viz., 114° . (Found : Eqt. wt, 225.4; C, 64.4; H, 7.3. $C_{12}H_{16}O_4$ requires eqt. wt. 224; C, 64.3; H, 7.1 per cent.).

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CONDENSATION OF O-METHOXY-PHENYL-SUCCINIC ANHYDRIDE WITH PHENOL METHYL ETHERS

By

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THE condensation of p-methoxy-phenyl-succinic anhydride with phenol ethers has already been reported. (Dalal, Bokil and Nargund, Journal Bombay University, 1939, vol. 8, part 3, page 190. Savkar, Bokil and Nargund, *ibid*, page 198). The present work is a continuation of similar work. The keto acids obtained in such condensations are to be converted into the corresponding γ -butyrolactones with a view to studying their anthelmintic action.

Although there is a possibility of getting two isomeric keto-butyric acids in the condensation of an unsymmetrically substituted succinic anhydride with phenol ethers, yet, in the present case, only one type of keto-acids could be isolated in crystalline condition. It is possible that the other type of keto-acids might have been formed but has eluded isolation so far. We have definite indication of the formation of two keto acids in the condensation of o-methoxy-phenyl-succinic anhydride with o-cresol-methyl ether and m-cresol-methyl ether. As the constitutions of these compounds are yet to be ascertained, an account of it will be given in the next communication. The present paper deals with condensation of o-methoxy-phenyl-succinic anhydride with anisole, p-cresol-methyl ether, veratrole, resorcinol dimethyl ether, resorcinol monomethyl ether, and hydroquinone dimethyl ether. Hydroquinone monomethyl ether and guaiacol did not condense with o-methoxy-phenyl-succinic anhydride. The structures of the keto acids have been proved in many cases by the synthesis from a suitable chalcone by Hahn and Lapworth's method. (J. C. S., 1904, 1358). All the keto acids obtained reacted with salicylaldehyde to give deep-red, pyrylium derivatives and also

reacted with piperonal to yield piperonylidene derivatives thus affording further proof of the constitutions assigned to them.

EXPERIMENTAL

The yields of the keto acids obtained in the condensation of o-methoxy-phenyl succinic anhydride with phenol methyl ethers using the general procedure described by Dalal, Bokil and Nargund (loc. cit.) are given in the following table.

TABLE

Phenol ether used	Product obtained	Yield per cent. of the product in different solvents
Anisole.	α -o-methoxy phenyl β -p-methoxy-benzoyl propionic acid.	50 in nitrobenzene. 25 in acetylene tetrachloride.
p-cresol-methyl ether.	α -o-methoxy-phenyl β -6-methoxy-3-toluoyl propionic acid.	83 in nitrobenzene. 50 in acetylene tetrachloride.
Veratrole.	α -o-methoxy-phenyl β -3-4-dimethoxy-benzoyl propionic acid.	57 in nitrobenzene. 57 in acetylene tetrachloride.
Resorcinol-dimethyl ether.	α -o-methoxy-phenyl β -2-4-dimethoxy-benzoyl propionic acid.	48 in nitrobenzene. 22 in acetylene tetrachloride.
Resorcinol mono methyl ether.	α -o-methoxy-phenyl β -2-hydroxy-4-methoxy benzoyl propionic acid.	15 in nitrobenzene 15 in acetylene tetrachloride.
Hydroquinone dimethyl ether.	α -o-methoxy-phenyl β -2-5-dimethoxy benzoyl propionic acid.	86 in nitrobenzene. 71 in acetylene tetrachloride.

α -o-methoxy-phenyl- β -p-methoxy-benzoyl propionic acid.—It was soluble in ethyl acetate, hot alcohol and hot acetic acid. It crystallised in needles from alcohol, m. p. 140° . (Found: C, 68.6; H, 5.7. Ag in silversalt, 24.5 per cent. $C_{18}H_{18}O_5$ requires C, 68.8; H, 5.7 per cent.). *Methyl- α -o-methoxy-phenyl- β -p-methoxy-benzoyl propionate* prepared by the action of methyl iodide on the silver salt of the acid, crystallised from alcohol in

needles, m. p. 83° . (Found: C, 69.5; H, 6.2, $C_{19}H_{20}O_5$ requires C, 69.5; H, 6.0 per cent.). *Ethyl- α -o-methoxy-phenyl- β -p-methoxy-benzoyl propionate* prepared similarly crystallised from petrol-benzene in granules, m.p. 96° . (Found: C, 70.4; H, 6.3. $C_{20}H_{22}O_5$ requires C, 70.2; H, 6.4 per cent.).

Synthesis of α -o-methoxy-phenyl- β -p-methoxy benzoyl propionic acid:—2; 4'-dimethoxy chalkone prepared from p-methoxy-acetophenone and o-methoxy benzaldehyde in presence of 50 per cent. sodium hydroxide was a pasty liquid which did not react with potassium cyanide. α -o-methoxy-phenyl- β -p-methoxy-benzoyl- α - β -dibromo ethane prepared from the above chalkone by adding the required quantity of bromine in carbondisulphide solution was a colourless solid crystallising in silky needles from benzene, m. p. 89° . (Found: Br. 37.4 per cent. $C_{17}H_{16}O_5Br_2$ requires Br. 37.9 per cent.) The bromo compound (1.0 gms.), potassium cyanide (0.5 gms.) and alcohol (16 cc.) were refluxed on water bath for two hours. Alcohol was then removed and the residue hydrolysed by heating with concentrated sulphuric acid (5 gms) and water (3 gms.) on sand bath for two hours. The product isolated had m.p. 139° and did not depress the m.p. of the product obtained by the condensation of o-methoxy-phenyl succinic anhydride with anisole.

α -o-methoxy-phenyl- β -6-methoxy-3-toluoyl propionic acid.—It was soluble in hot alcohol, benzene and hot acetic acid. It crystallised from dilute acetic acid in granules, m.p. 124° . (Found: C, 69.3; H, 6.3. Eqt. Wt. 324.5. $C_{19}H_{20}O_5$ requires C, 69.5; H, 6.0 per cent. Eqt. Wt. 328.). *Ethyl- α -o-methoxy-phenyl- β -6-methoxy-3-toluoyl propionate* prepared from the silver salt of the above acid and ethyl iodide crystallised from alcohol in needles, m.p. 105° . (Found: C, 70.5; H, 6.9. $C_{21}H_{24}O_5$ requires C, 70.8; H, 6.7 per cent.). The above acid could not be synthesised as 2; 2' dimethoxy 5'-methyl-chalkone could not be prepared.

α -o-methoxy-phenyl- β -3; 4-dimethoxy-benzoyl propionic acid.—It was soluble in ethyl acetate, hot alcohol, hot acetic acid, and hot chloroform. It crystallised from benzene-petrol mixture in rhombic plates, m.p. 127° . (Found: C, 66.0; H, 5.7. Eqt. Wt. 347.0. $C_{19}H_{20}O_5$ requires C, 66.3; H, 5.8 per cent. Eqt. Wt. 344.). *Methyl- α -o-methoxy-phenyl- β -3-4-dimethoxy-benzoyl propionate* prepared from the silver salt and methyl iodide crystallised in granules, m.p. 107° . (Found: C, 66.9; H, 6.2.

$C_{20}H_{12}O_5$ requires C, 67.1; 6.1 per cent.). *Ethyl- α -o-methoxy-phenyl- β -3; 4-dimethoxy-benzoyl propionate* prepared similarly crystallised from benzene-petrol mixture in minute needles, m.p. 75°. (Found: C, 67.4; H, 6.6. $C_{21}H_{14}O_6$ requires C, 67.7; H, 6.5 per cent.).

Synthesis of α -o-methoxy-phenyl- β -3-4-dimethoxy benzoyl propionic acid.—2:3':4'-trimethoxy chalcone prepared from acetoveratrone and o-methoxy-benzaldehyde was a pasty liquid. On adding the required quantity of bromine to the above chalcone there was obtained *α -o-methoxy-phenyl- β -3-4-dimethoxy-benzoyl- α - β -dibromo-ethane* which crystallised from acetic acid in granules, m.p. 170°. (Found: Br. 35.2. $C_{18}H_{16}O_4Br_2$ requires Br. 34.9 per cent.). Addition of potassium cyanide and hydrolysis of the resulting product was carried out as described in the case of anisole product. The keto acid isolated had m.p. 128° and was identical with the product obtained in the condensation of o-methoxy phenyl succinic anhydride with veratrole.

α -o-methoxy-phenyl- β -2-4-dimethoxy benzoyl-propionic acid.—It was soluble in hot alcohol, hot acetic acid, ethyl acetate but insoluble in chloroform. It crystallised in needles from acetic acid, m.p. 162°. (Found: C, 66.1; H, 6.1. Eqt. Wt. 347.0 $C_{19}H_{10}O_6$ requires C, 66.3; H, 5.8 per cent. Eqt. Wt. 344.) *Ethyl- α -o-methoxy-phenyl- β -2-4-dimethoxy-benzoyl propionate* prepared from the silver salt of the acid and ethyl iodide crystallised from alcohol in rhombic plates, m.p. 97°. (Found: C, 67.6; H, 5.1; $C_{21}H_{14}O_6$ requires C, 67.7; H, 6.5 per cent.).

Synthesis of the above acid.—2:2':4' trimethoxy chalcone prepared from resacetophenone dimethyl ether and o-methoxy-benzaldehyde in presence of 50 per cent. sodium hydroxide crystallised from alcohol in thin plates, m.p. 107°. (Found: C, 72.3 H, 6.2. $C_{18}H_{16}O_4$ requires C, 72.5; H, 6.0 per cent.). *α -o-methoxy phenyl- β -2: 4-dimethoxy-benzoyl- α - β -dibromo ethane* prepared from the above chalcone crystallised from acetic acid in granules, m.p. 171°. (Found: Br. 35.2. $C_{18}H_{16}O_4Br_2$ requires Br. 34.9 per cent.). The bromo compound on treatment with potassium cyanide and hydrolysis of the resulting product gave a keto acid, m.p. 159°, identical with the acid described above.

α -o-methoxy-phenyl- β -2-hydroxy-4-methoxy-benzoyl propionic acid.—It was first crystallised from acetic acid and then from ethyl alcohol in needles, m.p. 165°. It gave a bluish colouration with

alcoholic ferric chloride thus indicating that the side chain COCH_3 is in ortho position to OH group. On methylation with dimethyl sulphate and sodium hydroxide solution it gave an acid identical with that obtained by the condensation of resorcinol dimethyl ether with o-methoxy-phenyl-succinic anhydride. (Found: C, 65.8; H, 5.4; Eqt. Wt. 330. $\text{C}_{18}\text{H}_{18}\text{O}_6$ requires C, 65; H, 5.5 per cent. Eqt. Wt. 330). *Ethyl α -o-methoxy-phenyl- β -2-hydroxy-4-methoxy-benzoyl propionate* was prepared from the silver salt of the acid and ethyl iodide. It crystallised from alcohol in granules, m.p. 109. (Found: C, 67.0; H, 6.2. $\text{C}_{20}\text{H}_{22}\text{O}_6$ requires C, 67.0; H, 6.1 per cent.).

α -o-methoxy-phenyl- β -2.5-dimethoxy-benzoyl propionic acid.—It was soluble in hot alcohol, hot acetic acid, ethyl acetate. It crystallised from acetic acid in tiny plates, m.p. 141°. (Found: C, 66.0; H, 6.0. Eqt. Wt. 340.3. $\text{C}_{19}\text{H}_{20}\text{O}_6$ requires C, 66.3; H, 5.9 per cent.). *Methyl- α -o-methoxy-phenyl- β -2.5-dimethoxy-benzoyl propionate* prepared from the silver salt and methyl iodide, crystallised in needles from alcohol, m.p. 110°. (Found: C, 67.1; H, 6.0. $\text{C}_{20}\text{H}_{22}\text{O}_6$ requires C, 67.1; H, 6.1 per cent.).

Ethyl- α -o-methoxy-phenyl- β -2.5-dimethoxy-benzoyl propionate prepared similarly had m.p. 86°. (Found: C, 67.1; H, 6.6. $\text{C}_{21}\text{H}_{24}\text{O}_6$ requires C, 67.7; H, 6.5 per cent.).

Synthesis of α -o-methoxy-phenyl- β -2.5-dimethoxy-benzoyl propionic acid. 2.2'.5'-trimethoxy chalcone was prepared from 2.5-dimethoxy-acetophenone and o-methoxy benzaldehyde in presence of 10 per cent. sodium hydroxide at ordinary temperature. It crystallised in needles from alcohol, m.p. 77°. (Found: C, 72.3; H, 6.2. $\text{C}_{18}\text{H}_{18}\text{O}_4$ requires C, 72.5; H, 6.0 per cent.).

α -o-methoxy-phenyl- β -2.5-dimethoxy-benzoyl- α - β -dibromo ethane prepared from the above chalcone by adding the required quantity of bromine in carbon disulphide solution crystallised from acetic acid in rhombic plates, m.p. 137°. (Found: Br, 35.3. $\text{C}_{18}\text{H}_{18}\text{O}_4 \text{ Br}_2$ requires Br, 34.9 per cent.).

Addition of potassium cyanide and the hydrolysis of the addition product by concentrated sulphuric acid and water was carried out as described before. The keto acid obtained had m. p. 141° and did not depress the m.p. of the acid obtained in the condensation of o-methoxy-phenyl-succinic anhydride with hydroquinone dimethyl ether..

All the keto acids described in this paper reacted with salicylaldehyde and piperonal to give pyrylium and piperonylidene derivatives. Since these have not been analysed their description is not given here.

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SYNTHESIS OF γ -KETO-BUTYRIC ACIDS WITH METHOXY-PHENYL OR METHOXY TOLYL GROUPS AS SUBSTITUENTS IN α - AND γ -POSITIONS

By

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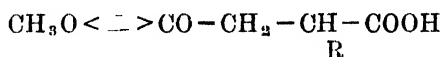
IN connection with synthetical anthelmintics a number of γ -keto-butyric acids have been prepared in this laboratory with a view to converting them into the corresponding γ -butyrolactones. (Dalal, Bokil and Nargund, Jour. Bom. Univ., 1939, Vol. 8, part 3, page 190. Savkar, Bokil and Nargund, *ibid.*, page 198. Savkar, Bokil and Nargund, preceding paper). A convenient method for preparing such keto acids has now been found, an account of which is given in the following pages.

Numerous examples have been reported of the use of aluminum chloride, or sulphuric acid or dry hydrogen chloride to bring about the addition reaction between an unsaturated substance and benzene, toluene, phenol, resorcinol and hydroquinone. (Claisan, German Patent, 1923, 374142. Libermann and Hartmann. B. 24, 2582; B. 25, 957. König. B. 24, 3889. Eijkmann. Chem. Centr. 1907, II, 2045; *ibid.* 1908, II, 1100. Kohler. Amer. Chem. Jour. 1904, 31, 642; *ibid.* 1909, 42, 379. Niederl and coworkers, several papers in Jour. Amer. Chem. Soc.). Rice (J. A. C. S., 1931, 53, 3153) in an attempt to condense maleic anhydride with resorcinol dimethyl ether obtained in addition to two other substances, an acid which can be described as α -2,4-dimethoxy-phenyl- β -2,4-dimethoxy benzoyl propionic acid. The formation of this substance was explained as due to the addition of resorcinol dimethyl ether to β -(2,4-dimethoxy benzoyl) acrylic acid which is expected to be the primary product in the condensation of maleic anhydride with resorcinol dimethyl ether. Pummerer and Bucta (B, 1936, 1006) reported that benzene and toluene could be added to β -benzoyl acrylic acid or β -p-tolyl acrylic acid. We have now found that β -p-

methoxy benzoyl acrylic acid smoothly adds on phenol ethers to yield disubstituted γ -keto-butyric acids.

Neither anhydrous aluminium chloride nor dry hydrogen chloride was successful to bring about the addition of phenol ethers to β -p-methoxy-benzoyl acrylic acid. Concentrated sulphuric acid at ordinary temperatures (35°) brought about sulphonation of β -p-methoxy-benzoyl acrylic acid. It was, however, found that phenol ethers could be smoothly added to β -p-methoxy-benzoyl acrylic acid in presence of 80 per cent. sulphuric acid.

The addition of a phenol ether to β -p-methoxy-benzoyl acrylic acid is expected to give an acid of the following type.



That the keto-acids obtained by the addition of phenol ethers to β -p-methoxy-benzoyl acrylic acid have the above formula has been definitely established by an independent synthesis of the same keto acids from suitable chalkones following the method of Hahn and Lapworth. (J. C. S., 1904, 1358). Other evidences for assigning the above structures to the keto acids are : (i) All the keto acids readily reacted with salicyl aldehyde in presence of dry hydrogen chloride to give deep red pyrylium derivatives thus indicating the presence of COCH_2 -grouping. (ii) All the keto acids reacted with piperonal to yield gummy piperonylidene derivatives again pointing to the same inference as stated above.

EXPERIMENTAL

General procedure for the addition of phenol ethers to β -p-methoxy-benzoyl acrylic acid.— β -p-methoxy-benzoyl acrylic acid (Dave and Nargund, Jour. Bom. Univ., 1938, Vol. 7, part 3, page 192) (0.1 mol) was dissolved in 80 per cent. sulphuric acid (80 gms) and cooled in a water bath. Phenol methyl ether (0.1 mol) was then gradually added. It was kept at room temperature for two hours and then decomposed by addition of ice. The unused phenol ether was removed by steam distillation and β -p-methoxy-benzoyl acrylic acid was removed by repeatedly washing it with hot water. The residue was filtered, washed and dried. The yields obtained by the above procedure are given in the following table :—

Addition of phenol methyl ethers to β -p-methoxy-benzoyl acrylic acid.

Phenol ether used	Product obtained	Yield of the product
Anisole	α -p-methoxy-phenyl- β -p-methoxy-benzoyl propionic acid.	50 per cent.
O cresol methyl ether	α -4-methoxy-3-tolyl- β -p-methoxy-benzoyl propionic acid.	92 per cent.
M cresol methyl ether	α -4-methoxy-2-tolyl- β -p-methoxy-benzoyl propionic acid.	70 per cent.
P cresol methyl ether	α -6-methoxy-3-tolyl- β -p-methoxy-benzoyl propionic acid.	28 per cent.
Veratrole	α -3 : 4 - dimethoxy - phenyl - β - p - methoxy-benzoyl propionic acid.	25 per cent.
Resorcinol dimethyl ether.	α -2 : 4 - dimethoxy - phenyl - β - p - methoxy-benzoyl propionic acid.	12 per cent.
Hydroquinone dimethyl ether.	Did not give any crystalline product.	
Resorcinol mono methyl ether.	Did not give any crystalline product.	
α - Naphthol - methyl ether.	α -4-methoxy-1-naphthyl- β -p-methoxy-benzoyl propionic acid.	72 per cent.
β - Naphthol - methyl ether.	α -2-methoxy-1-naphthyl- β -p-methoxy-benzoyl propionic acid.	57 per cent.

α -p-methoxy-phenyl- β -p-methoxy-benzoyl propionic acid.—It had m.p. 163° and was identical (mixed m.p.) with the acid described by Dalal, Bokil and Nargund (loc. cit.).

α -4-methoxy-3-tolyl- β -p-methoxy-phenyl propionic acid.—It was soluble in chloroform, benzene, ethyl acetate and hot alcohol

but insoluble in petroleum ether. It crystallised from alcohol in granules, m.p. 179° . (Found: equivalent wt. 330.8; C, 69.6; H, 6.3. Ag in silver salt, 25.1. $C_{15}H_{20}O_5$ requires equivalent wt. 328. C, 69.5; H, 6.1 per cent. $C_{15}H_{19}O_5Ag$ requires Ag, 24.8 per cent.).

Synthesis of the above acid.—4-4'-dimethoxy-3-methyl chalcone was prepared by the condensation of p-methoxy-acetophenone (Gattermann, Erhardt and Maisch B, 23, 1201) (6 gms) 4-methoxy-5-methyl-benzaldehyde (6 gms) alcohol (20 cc) in presence of 40 per cent. sodium hydroxide (12 gms) on water bath for ten minutes; yield 10 gms. It was soluble in benzene, chloroform, ethyl acetate, acetic acid and hot alcohol. It crystallised from alcohol in thick needles, m.p. 86° . (Found: C, 76.4; H, 6.5. $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4 per cent.). The above chalcone was characterised by the preparation of α -p-methoxy-benzoyl- β -4-methoxy-3-tolyl- α - β -dibromo ethane by adding the requisite quantity of bromine in carbondisulphide solution. It had m.p. 122 with decomposition. (Found: Br, 36.6. $C_{18}H_{18}O_3Br_2$ requires Br, 36.2 per cent.); 4:4-dimethoxy 3-methyl chalcone (3 gms) was dissolved in alcohol (50 cc) and a solution of potassium cyanide (1.3 gms) in water (4 cc) was added. After shaking it well, glacial acetic acid (0.6 cc) was added and left at room temperature for 24 hours. It was heated on water bath for three hours and alcohol removed by distillation and the residue washed with water. It was then hydrolysed by adding to it concentrated sulphuric acid (15 gms) and water till there was slight turbidity (about 10 cc) and boiling it on sand bath for three hours. The product after purification by sodium carbonate and recrystallisation from alcohol had m.p. 179° and did not depress the m.p. of the product obtained by the addition of o-cresol-methyl ether to β p-methoxy-benzoyl acrylic acid.

α -4-methoxy-2-tolyl- β -p-methoxy-benzoyl propionic acid.—It was soluble in alcohol, acetic acid, benzene, chloroform and ethyl acetate. It crystallised from ethyl acetate after one day in rhombic plates and had m.p. 132° . (Found: Eqt. wt. 332.4; C, 69.6; H, 6.5 Ag in silver salt, 25.2. $C_{19}H_{20}O_5$ requires eqt. wt. 328. C, 69.5; H, 6.1 per cent. $C_{19}H_{19}O_5Ag$ requires Ag, 24.8 per cent.)

Synthesis of the above acid.—4-4'-dimethoxy-6-methyl chalcone was prepared by heating together p-methoxy-acetophenone (7 gms), 4-methoxy-2-methyl benzaldehyde (7 gms), alcohol (30 cc) and 50 per cent. sodium hydroxide (14 gms) on water bath for ten minutes; yield 11 gms. It was soluble in the

usual solvents and crystallised from alcohol in yellow needles, m.p. 117–118°. (Found : C, 76.3; H, 6.7. $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4 per cent.). α -*p*-methoxy-benzoyl- β -4-methoxy-2-tolyl- α - β -dibromo ethane prepared from the chalkone crystallised from acetic acid in hexagonal plates, m.p. 116° with decomposition. (Found : Br, 36.6. $C_{18}H_{18}O_3Br_2$ requires Br, 36.2 per cent.). Addition of hydrogen cyanide and the hydrolysis of the resulting cyano compound were carried out as described in the former case. The product obtained crystallised in rhombic plates from ethylacetate and had m.p. 132° and was identical with the product obtained by the addition of *m*-cresol-methyl ether to β -*p*-methoxy-benzoyl acrylic acid.

α -6-methoxy-3-tolyl- β -*p*-methoxy-benzoyl propionic acid.—It was soluble in chloroform, benzene, ethyl acetate acetic acid and hot alcohol. It crystallised from alcohol in plates, m.p. 140–141°. (Found : Eqt. wt. 324.4; C, 69.3; H, 6.3. $C_{19}H_{20}O_5$ requires eqt. wt. 328. C, 69.5; H, 6.1 per cent.).

Synthesis of the above acid.—2,4'-dimethoxy-5-methyl chalkone prepared from *p*-methoxy-acetophenone (12 gms), 6-methoxy-3-methyl benzaldehyde (12 gms), alcohol (60 cc) and 0 per cent. sodium hydroxide (24 gms) as described before. It was a pale yellow solid soluble in the usual solvents and crystallised from alcohol in star-shaped crystals, m.p. 102–103°. (Found : C, 76.5; H, 6.7. $C_{18}H_{18}O_3$ requires C, 76.9; H, 6.4 per cent.). α -6-methoxy-3-tolyl- β -*p*-methoxy-benzoyl- α - β -dibromo-ethane prepared from the above chalkone by adding the requisite quantity of bromine in carbondisulphide solution was a sticky mass. The addition of hydrogen cyanide and the hydrolysis of the resulting product were carried out as described before. The keto acid obtained was identical with that obtained by the addition of *p*-cresol-methyl ether to *p*-methoxy-benzoyl propionic acid.

α -3,4-dimethoxy-phenyl- β -*p*-methoxy-benzoyl propionic acid.—It was soluble in acetic acid and hot alcohol and sparingly soluble in benzene, chloroform and ethyl acetate. It crystallised from alcohol in needles, m.p. 180°. (Found : Eqt. wt. 343.2; C, 66.2; H, 5.8. $C_{19}H_{20}O_6$ requires eqt. wt. 344; C, 66.3; H, 5.8 per cent.).

Synthesis of the above acid.—3,4':4-trimethoxy chalkone was prepared by treating veratraldehyde (3 gms), *p*-methoxy-acetophenone (3 gms), alcohol (15 cc) and 50 per cent. sodium hydroxide (6 gms) in the usual manner yield 2 gms. It was

soluble in the usual solvents and crystallised from alcohol like branched needles, m.p. 96–98°. (Found: C, 72.7; H, 6.3. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.0 per cent.). Addition of hydrogen cyanide and hydrolysis in the usual manner furnished a keto acid, m.p. 180, identical with the acid described above.

α -2:4-dimethoxy-phenyl- β -p-methoxy-benzoyl propionic acid.

—It was soluble in alcohol, acetic acid, ethyl acetate, chloroform and hot benzene. It crystallised from benzene in branched needles, m.p. 128°. (Found: Eqt. wt. 341.8; C, 66.3; H, 5.8. $C_{19}H_{20}O_6$ requires eqt. wt. 344; C, 66.3; H, 5.8 per cent.).

Synthesis of the above acid.—2:4':4-trimethoxy-chalkone was prepared from 2:4-dimethoxy-benzaldehyde and p-methoxy-acetophenone in the usual manner. It was soluble in benzene, chloroform, ethyl acetate, hot alcohol and hot acetic acid. It crystallised from alcohol in clusters of needles, m.p. 82°. (Found: C, 72.2; H, 6.2. $C_{18}H_{18}O_4$ requires C, 72.5; H, 6.0 per cent.). The above chalkone readily added on hydrogen cyanide under the usual conditions and the hydrolysis of the resulting product by concentrated sulphuric acid gave a keto acid, m.p. 129°. It did not depress the m.p. of the product obtained by the addition of resorcinol dimethyl ether to β -p-methoxy-benzoyl acrylic acid.

α -4-methoxy-1-naphthyl- β -p-methoxy-benzoyl propionic acid.

—It was soluble in alcohol, acetic acid, chloroform, ethyl acetate and hot benzene. It crystallised from benzene in granules, m.p. 151–152°. (Found: Eqt. wt. 371.4; C, 72.4; H, 6.8. $C_{22}H_{20}O_5$ requires eqt. wt. 364; C, 72.5; H, 5.6 per cent.). This acid could not be synthesised as the corresponding chalkone could not be obtained under the usual conditions. The above structure assigned to the acid, therefore, rests on general grounds. That this acid contained a grouping like $COCH_2$ was shown by the preparation of a pyrylium derivative. The acid was characterised by the preparation of the following derivatives. *Methyl- α -4-methoxy-1-naphthyl- β -p-methoxy-benzoyl propionate* was prepared by esterifying the acid by Fischer-Speier method. It was soluble in chloroform, acetic acid, ethyl acetate and sparingly soluble in benzene and alcohol. It crystallised from benzene in needles, m.p. 106°. (Found: C, 72.7; H, 5.8. $C_{23}H_{22}O_5$ requires C, 73.0; H, 5.8 per cent.). *Ethyl- α -4-methoxy-1-naphthyl- β -p-methoxy-benzoyl propionate* prepared similarly crystallised from benzene in prisms, m.p. 110°. (Found: C, 73.6; H, 6.4. $C_{24}H_{24}O_5$ requires C, 73.4; H, 6.1 per cent.).

α -2-methoxy-1-naphthyl- β -p-methoxy-benzoyl propionic acid.

—It was soluble in alcohol, acetic acid, ethyl acetate, benzene, chloroform and sparingly soluble in ether and petroleum ether. It could not be crystallised from any solvent. It had m.p. 120–125°. It, however, gave correct results on analysis. (Found: Eqt. wt. 358.4; C, 72.1; H, 5.6. $C_{22}H_{20}O_5$ requires eqt. wt. 364. C, 72.5; H, 5.6 per cent.). The above acid could not be synthesised and hence its constitution could not definitely be established. In common with other keto acids it also gave a pyrylium derivative.

All the keto acids described in this paper gave on treatment with salicylaldehyde deep-red pyrylium derivatives and with piperonal piperonylidene derivatives. But as these compounds have not been analysed a description of these is not given here.

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A STUDY OF THE REDUCTION PRODUCTS OF CHLORAL-HYDROXY-BENZOIC ACIDS

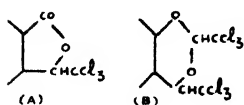
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MELDRUM and his coworkers have observed that the $\text{CHOH} \cdot \text{CCl}_3$ group, trichloromethylphthalide ring (A) and the heterocyclic ring (B)



present among the chloral condensation products of hydroxy-benzoic acids can be converted into the CH_2CHCl_2 group on reduction with zinc dust and acetic acid (Meldrum

and Alimchandani, J. C. S., 1921, 204; J. Indian Chem. Soc., 1929, 253; Shah and Alimchandani, *ibid.*, 1931, 261; (late) Meldrum and Hurry, *ibid.*, 1934, 535; Meldrum and Parikh, Proc. Indian Acad. Sci., 1935, I, 431; Meldrum and Vaidyanathan, *ibid.*, 1935, I, 510). In the present work, however, it has been found that the reduction products have the unsaturated constitution R-CH:CCl_2 and not $\text{R-CH}_2\text{CHCl}_2$ (R =benzene residue). Thus the compounds from chloral with salicylic acid, *p*- and *m*-hydroxybenzoic acids, *viz.*, 2-hydroxy-5- α -hydroxy- $\beta\beta\beta$ -trichloroethylbenzoic acid (I; Calvet and Mejuto, J. C. S., 1936, 554), 6-carboxy-2:4-bistrichloromethyl-1:3-benzdioxin (II; Chattaway and Prats, J. C. S., 1929, 685) and 5-hydroxy-trichloromethyl-phthalide (III; Chattaway and Calvet, J. C. S., 1928, 1092) on reduction with zinc and acetic acid gave 2-hydroxy-5- $\beta\beta$ -dichloro-, 4-hydroxy-5- $\beta\beta$ -dichloro- and 3-hydroxy-6- $\beta\beta$ -dichloro-vinylbenzoic acids, (IV), (V) and (VI) respectively of the general formula R-CH:CCl_2 . Similar reduction products were obtained from chloral and bromal-amides by Yelburgi and Wheeler (J. Indian Chem. Soc., 1934, 217; *vide* also (late) Meldrum and Vad, *ibid.*, 1936, 117; *et seq.* and Bhojraj, *ibid.*, 1936, 185). These authors have shown that in the chloral and bromal-amides the group- $\text{CHOH} \cdot \text{CX}_3$ was reduced to -CH:CX_2 and not to $\text{-CH}_2\text{CHX}_2$ (X =halogen).

The constitution of (IV) and (V) is also further confirmed by an independent synthesis from 2-hydroxy- and 4-hydroxy-5- $\alpha\beta\beta\beta$ -tetrachloroethylbenzoic acids (J. Indian Chem. Soc.,

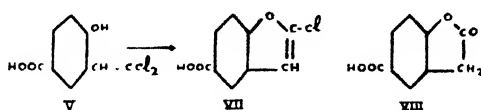
1940, 417) by the action of potassium iodide (*cf.* van Duin, *Rec. Trav. Chim.*, 1926, 45, 345; Dillong and his co-workers, *J. Am. Chem. Soc.*, 1930, 52, 1953). The reaction being definitely unambiguous, proves beyond doubt the unsaturated structure of the reduction products. Methylation of (IV), (V) and (VI) yielded compounds which were identical with the reduction products derived directly from methoxy-salicylic acid, anisic acid and *m*-methoxy-benzoic acid respectively, which, however, have been inadvertently assigned the saturated constitution by the previous investigators (Hurry and Meldrum, *loc. cit.*) who depended solely on the analysis of chlorine only. It will be evident from the following table that it is the analysis of carbon and hydrogen and not chlorine only that can decide the saturated or the unsaturated constitution of the products under reference :—

Redn. Product derived from	Author and reference	C	Found H	Cl
1. Salicylic acid.	Calvet and Mejuto (J., 1936, 556). Dharwarkar and Alimchandani.	46.3 46.53	2.8 2.73	... 30.10
2. <i>p</i> -hydroxy-benzoic acid.	Do.	46.43	2.77	30.23
3. <i>m</i> -hydroxy-benzoic acid.	Hurry and Meldrum (<i>loc. cit.</i>). Dharwarkar and Alimchandani.	... 46.42	... 2.71	30.2 ...
(Sat : formula $C_9H_8O_3Cl_2$ requires C, 45.97; H, 3.43; Cl, 30.16 per cent.). (Unsat : formula $C_9H_6O_3Cl_2$ requires C, 46.35; H, 2.6; Cl, 30.44 per cent.).				
4. Methoxy-salicylic acid.	Hurry and Meldrum (<i>loc. cit.</i>). *Shah and Alimchandani (<i>J. Ind. Chem. Soc.</i> , 1936, 475). Dharwarkar and Alimchandani.	... 48.22 48.81	... 3.63 3.37	28.3 28.35 ...
5. Anisic acid.	Hurry and Meldrum (<i>loc. cit.</i>). Dharwarkar and Alimchandani.	... 48.77	... 3.32	28.3 ...
6. <i>m</i> -methoxy-benzoic acid.	Hurry and Meldrum (<i>loc. cit.</i>). Dharwarkar and Alimchandani.	... 48.74	... 3.35	28.6 ...
(Sat : formula $C_{10}H_{10}O_3Cl_2$ requires C, 48.21; H, 4.04; Cl, 28.5 per cent.). (Unsat : formula $C_{10}H_8O_3Cl_2$ requires C, 48.6; H, 3.26; Cl, 28.69 per cent.).				

* The percentage of C found by these authors agrees with the saturated constitution, the percentage of H, however, lies midway between the saturated and the unsaturated constitution. It is very likely that the analysis is not accurate.

These reduction products, though unsaturated, do not form any addition compounds with dry hydrochloric acid gas or bromine as was observed in the case of those obtained from chloral—and bromal—amides by Yelburgi and Wheeler (loc. cit.).

On hydrolysis with dilute alkali, the compound (V) gave 5-carboxy-2-chloro-coumarone (VII) (cf. Lonkar and Meldrum, J. Univ. of Bombay, 1937, 116) and compound (VI) gave a bright yellow crystalline product, m.p. 215° (decomp.) the constitution of which is under investigation, while the compound (IV) yielded a tarry mass. The methoxy compounds, however, yielded derivatives of β -chloro-phenyl-acetylene ($R-C\equiv Cl$). The β -chlorophenylacetylene from methoxy-salicylic acid adds on HCl giving 4-methoxy-5-carboxy-1- $\alpha\beta$ -dichlorostyrene.



Treatment with hot concentrated sulphuric acid converts all the reduction products into the corresponding phenylacetic acids, ($R-CH_2COOH$). The phenylacetic acid derived from *p*-hydroxybenzoic acid on heating loses a molecule of water forming the lactone (VIII).

EXPERIMENTAL

2-hydroxy-5- $\beta\beta$ -dichlorovinylbenzoic acid (IV)

2-hydroxy-5- α -hydroxy- $\beta\beta\beta$ -trichloroethylbenzoic acid (Calvet and Mejuto, loc. cit. ; 6 gm.) was dissolved in glacial acetic acid (60 cc) and zinc dust (3 gm.) was gradually added to the warm solution. After the reaction was over, the solution was filtered, diluted with water and the product obtained was crystallised from benzene, silky needles, m.p. 170°. Yield 4 gm.

It does not absorb bromine but potassium permanganate is easily decolourised in cold alcoholic solution. Ferric chloride produces deep blue colouration. (cf. Calvet and Mejuto, loc. cit.). (Found : C, 46.53 ; H, 2.73 ; Cl, 30.10. $C_9H_6O_3Cl_2$ requires C, 46.35 ; H, 2.6 ; Cl, 30.44%).

Acetyl derivative crystallised from chloroform in tiny needles, m.p. 126°. (Found : Cl, 25.68. $C_{11}H_8O_4Cl_2$ requires Cl, 25.77%).

Benzoyl derivative crystallised from benzene-petroleum benzine in needles, m.p. 140°. (Found : Cl, 20.93. $C_{16}H_{10}O_4Cl_2$ requires Cl, 21.04%).

4-hydroxy-5-carboxy-phenylacetic acid

The reduction product (IV; 5 gm.) was heated with conc. sulphuric acid (30 cc) on water bath with constant stirring at 75°—80°C. After the reaction was over the mixture was cooled and poured over ice and extracted with ether. The residue recovered was crystallised from a mixture of ethylacetate and petroleum benzine in rhombic plates, m.p. 207°—8°. Ferric chloride produces violet colouration. (Found: C, 54.97; H, 4.23; Equiv., 97.74. $C_9H_8O_5$ requires C, 55.09; H, 4.11; Equiv., 98.08. The silver salt gave Ag., 52.35%. $C_9H_8O_5Ag_2$ requires Ag., 52.48%).

The same compound was also obtained by demethylating 4-methoxy-5-carboxy-phenylacetic acid (1 gm.; Shah and Alimchandani, J. Indian Chem. Soc., 1936, 477) with hydriodic acid (2 gm).

4-hydroxy-5-ββ-dichlorovinylbenzoic acid (V)

6-carboxy-2:4-bistrichloromethyl-1:3-benzdioxin (10 gm; Chattaway and Prats, J. C. S., 1929, 685) was dissolved in glacial acetic acid (40 cc) and zinc dust (14 gm.) was added gradually over 4 hours with continuous shaking and occasional cooling. The mixture was filtered and diluted with water (100 cc) and evaporated on water bath to a small bulk. On keeping overnight the reduction product separated in long needles along with some tarry mass. It was crystallised first from boiling water (charcoal) and then from a mixture of benzene and petroleum benzine in needles, m.p. 171°—72°. Yield 2 gm. Alcoholic ferric chloride produces a feeble purple colouration. (Found: C, 46.43; H, 2.77; Cl, 30.23; $C_9H_6O_5Cl_2$ requires C, 46.35; H, 2.6; Cl, 30.44%).

The acetyl derivative was crystallised from chloroform in white soft needles, m.p. 191°—92°. (Found: Cl, 25.6. $C_{11}H_8O_4Cl_2$ requires Cl, 25.77%).

5-carboxy-2-chloro-coumarone (VII)

The above mentioned reduction product (V; 2 gm.) was dissolved in 50% sodium hydroxide (25 cc) and heated on water bath for 15 minutes. The crystalline sodium salt which separated was filtered off and treated with dilute hydrochloric acid. The acid liberated was crystallised twice from acetone in soft tiny needles, m.p. 242°—43°. It is sparingly soluble in rectified spirit, chloroform and benzene. Ferric chloride produces no

colouration. (Found : C, 54.92; H, 2.66; Cl, 18.02. $C_9H_5O_5Cl$ requires C, 54.98; H, 2.56; Cl, 18.04%).

Calcium salt crystallises in rhombic plates with 5 molecules of water of which 2 molecules are lost at 110° — 120° . (Found : Ca, 7.72; $(C_9H_4O_5Cl)_2Ca \cdot 5H_2O$ requires Ca, 7.69%. After heating at 110° — 120° to constant weight, found : Ca, 8.61; $(C_9H_4O_5Cl)_2Ca \cdot 3H_2O$ requires Ca, 8.26%).

2-hydroxy-5-carboxy-phenylacetic acid

The reduction product (V; 4 gm.) was treated with conc. sulphuric acid (20 cc) at 70° — $80^\circ C$. After the reaction was over the dark brown solution was poured over ice and the product obtained was crystallised from a mixture of methyl-alcohol and benzene in needles, m.p. 186° (efferv.). Ferric chloride produces purple colouration. (Found : Equiv., 98.46; $C_9H_5O_5$ requires equiv., 98.08; The *silver* salt gave Ag., 52.44; $C_9H_5O_5Ag_2$ requires Ag., 52.48%).

Lactone of 2 hydroxy-5-carboxy-phenylacetic acid (VIII)

The above mentioned phenylacetic acid, m.p. 186° , was heated in a paraffin bath at 195° — 200° . When the effervescence was over, the fused mass was crystallised from a mixture of ethylacetate and petroleum benzine in rhombic plates, m.p. 232° — 33° . Ferric chloride produces no colouration. (Found : C, 60.67; H, 3.42. $C_9H_5O_4$ requires C, 60.7; H, 3.39%. *Silver* salt gave Ag., 37.74; $C_9H_5O_4Ag$ requires Ag., 37.87%).

3-hydroxy-6-β-dichlorovinylbenzoic acid (VI)

5-hydroxy-trichloromethyl-phthalide (5 gm; Chattaway and Calvet, J.C.S., 1928, 1092) was reduced with zinc dust (3 gm.) in glacial acetic acid (30 cc) in the usual manner and the product obtained was crystallised from methyl alcohol in needles, m.p. 196° — 97° . Hurry and Meldrum give m.p. 194° . (Found : C, 46.42; H, 2.71. $C_9H_6O_5Cl_2$ requires C, 46.35; H, 2.6%).

The *acetyl* derivative crystallised from rectified spirit in silky needles, m.p. 170° — 71° . (Found : Cl, 25.7; $C_{11}H_8O_4Cl_2$ requires Cl, 25.77%).

4-hydroxy-6-carboxy-phenylacetic acid

The compound VI (7 gm.) was added to conc. sulphuric acid (temp., $34^\circ C$.) when instantaneously the reaction started with evolution of hydrochloric acid gas. When it was over, the

solution was heated on water bath at 50° — 60° for a few minutes and poured over ice. The product was crystallised first from water (charcoal) and then from a mixture of methyl alcohol and petroleum benzene in yellowish short needles, m.p. 215° (efferv.). (Found : C, 55.24 ; H, 4.19 ; equiv., 98.06. $C_9H_8O_3$ requires C, 55.09 ; H, 4.11 ; equiv., 98.08. Silver salt gave Ag., 52.51 ; $C_9H_8O_3Ag_2$ requires Ag., 52.48%).

2-methoxy-5- $\beta\beta$ -dichlorovinylbenzoic acid

The reduction product, m.p. 134° , of 4-methoxy-5-carboxy-1- α -hydroxy- $\beta\beta\beta$ -trichloroethylbenzene (Hurry and Meldrum, loc. cit.; Shah and Alimchandani, J. Indian Chem. Soc., 1936, 475) was analysed for carbon and hydrogen and the results agree with the unsaturated formula. (Found : C, 48.81 ; H, 3.37. $C_{10}H_8O_3Cl_2$ (unsat.) requires C, 48.6 ; H, 3.26 ; $C_{10}H_{10}O_3Cl_2$ (Sat.) requires C, 48.21 ; H, 4.04%).

The same compound was also obtained by methylating the hydroxy compound IV by means of dimethyl sulphate.

4-methoxy-5-carboxy-phenyl- β -chloroacetylene

The above mentioned compound, m.p. 134° , was dissolved in 10% sodium hydroxide (45 cc) and refluxed on water bath for half an hour. The sodium salt separated was filtered off and treated with dilute hydrochloric acid. The product obtained was crystallised first from glacial acetic acid and then from rectified spirit in needles, m.p. 175° . (Found : C, 57.16 ; H, 3.62 ; Cl, 16.8. $C_{10}H_7O_3Cl$ requires C, 57.02 ; H, 3.35 ; Cl, 16.84%).

4-methoxy-5-carboxy-1- $\alpha\beta$ -dichlorostyrene

The phenylacetylene derivative (2 gm.) was dissolved in absolutely dry chloroform (50 cc) and saturated with dry hydrochloric acid gas. The bottle was kept sealed with paraffin for a week. On evaporation of the chloroform the substance separated in needles which were recrystallised from benzene, m.p. 145° . (Found : C, 48.84 ; H, 3.21 ; Cl, 28.61. $C_{10}H_8O_3Cl_2$ requires C, 48.6 ; H, 3.26 ; Cl, 28.69%).

4-methoxy-5- $\beta\beta$ -dichlorovinylbenzoic acid

2-methoxy-5-carboxy-1- α -hydroxy- $\beta\beta\beta$ -trichloroethylbenzene (Chattaway and Calvet, loc. cit.) (3 gm.) was reduced in the usual manner by zinc dust (2.5 gm.) in glacial acetic acid (60 cc). The compound crystallised from rectified spirit in

fine soft silky needles, m.p. 226° - 27° . Hurry and Meldrum (loc. cit.), however, report that it shrinks at 210° and melts at 222° . (Found: C, 48.77; H, 3.32. $C_{10}H_8O_3Cl_2$ requires C, 48.6; H, 3.26 %).

2-methoxy-5-carboxy-phenyl- β -chloro-acetylene

The above reduction product (5 gm.) was refluxed with 20% sodium hydroxide (50 cc) on water bath for 45 minutes. The precipitate obtained on acidification was first crystallised from glacial acetic acid and then from rectified spirit in yellowish tiny needles, m.p. 219° - 20° . Yield 2 gm. (Found: C, 57.18; H, 3.41 Cl, 16.77. $C_{10}H_7O_3Cl$ requires C, 57.02; H, 3.35; Cl, 16.84%).

2-methoxy-5-carboxy-phenylacetic acid

4-methoxy-5- $\beta\beta$ -dichlorovinylbenzoic acid (5 gm.) was heated with conc. sulphuric acid at 60° - 80° in the-usual manner. After the reaction was over, the product obtained on pouring the solution on ice crystallised from rectified spirit in short needles, m.p. 264° - 65° . Yield 3gm. (Found: Equiv., 105.0. $C_{10}H_{10}O_6$ requires equiv., 105.09. Silver salt gave Ag., 50.86. $C_{10}H_8O_5Ag_2$ requires Ag., 50.91%).

Demethylation with hydrodic acid yielded 2-hydroxy-5-carboxy-phenylacetic acid, m.p. 186° , which was confirmed by mixed m.p. determination.

3-methoxy-6- $\beta\beta$ -dichlorovinylbenzoic acid

5-methoxy-trichloromethylphthalide (Fritsch, Ann., 1897, 296, 344) was reduced with zinc dust and acetic acid in an identical manner described by Hurry and Meldrum (loc. cit.). The product was crystallised from rectified spirit in needles, m.p. 167° - 68° . The m.p. reported by the above authors is, however, 164° . (Found: C, 48.74; H, 3.35. $C_{10}H_8O_3Cl_2$ requires C, 48.6; H, 3.26%).

The compound is also obtained by methylating 3-hydroxy-6- $\beta\beta$ -dichlorovinylbenzoic acid (2 gm.) with dimethyl sulphate (5 cc) in sodium hydroxide solution (5%; 25 cc).

A NOTE ON THE REDUCTION OF SUBSTITUTED MALONATES

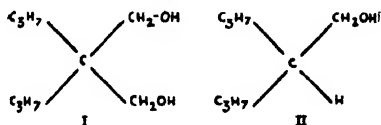
By

A. H. BHATKHANDE, N. L. PHALNIKAR AND B. V. BHIDE

THE object of the present work was to reduce dialkyl malonic esters and to obtain dialkyl trimethylene glycols with a view to determining the dipole moments and to test the valency Deflexion hypothesis (Ingold, J. C. S., 1921, 229) with respect to them. The method of reduction was the Bouveault method as modified by Mrs. Robinson (J. C. S., 1924, 229).

To start with, Diethyl di-*n*-propyl malonate was taken for reduction. It was found that the major part of the substance obtained on reduction was not the expected glycol (I), but was di-*n*-propyl ethanol (II). Hence in the reduction of malonate one carbethoxy group is eliminated. Both the acetyl and *p*-nitro benzoyl derivatives of di-*n*-propyl-ethanol (II) were liquids. After distillation a highly viscous liquid was left which could not be distilled without decomposition. It could not be also induced to crystallise. Hence it could not be further investigated.

Further work on the reduction of esters of substituted malonic and other dibasic acids is in progress.



EXPERIMENTAL

15 gm. of sodium were heated upto 140° in a three way round bottomed flask under reflux, and a mixture of 6.5 gm. of the ester and 50cc. of absolute alcohol was dropped on the melted, sodium, the addition being

continued for half an hour. The temperature was gradually raised upto 170°C and was maintained constant. 25cc. of absolute alcohol were then dropped in, and the refluxing was continued for 3 hours, the temperature being kept at 170°C . On cooling, water was added, the solution acidified with hydrochloric acid, and the oily layer which separated was extracted with ether. The ether extract was then dried and the ether was removed. The residue was distilled under vacuum and the portion boiling at $95-100^{\circ}\text{C}$ at 10mm. pressure was collected. The yield of di-n-propyl ethanol was 35% of the theoretical.

The molecular weight of the substance was determined by Ebullioscopic method in acetone.

(Mol. wt. found 126.1, $\text{C}_8\text{H}_{18}\text{O}$ requires 130).

(Found: C, 72.95% and H, 13.6%. $\text{C}_8\text{H}_{18}\text{O}$ requires C, 73.84%. H, 13.84%).

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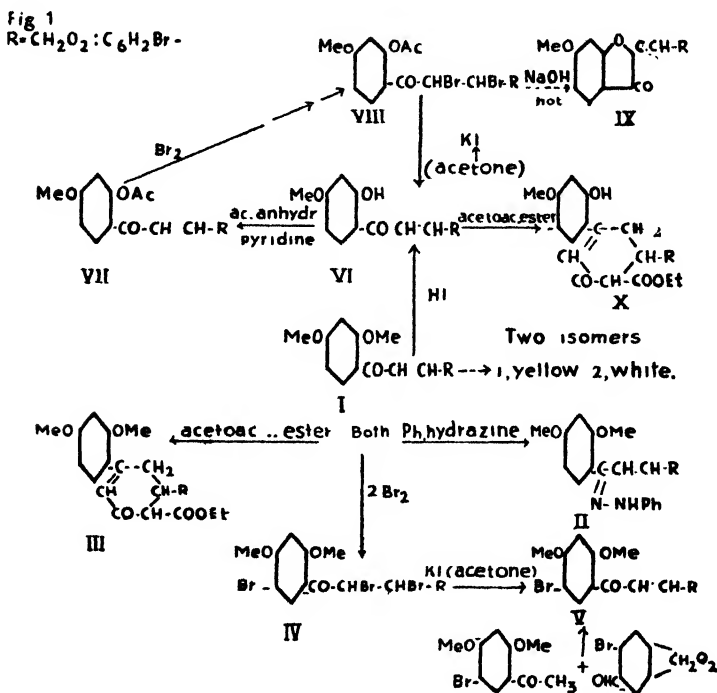
[Received July 21, 1940]

REACTIVITY OF ARYL P-ALKOXYSTYRYL KETONES

By

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THE paper comprises a study of the reactivities of some *p*-alkoxystyryl ketones; the sequence of reactions will be clear from the diagrams:—

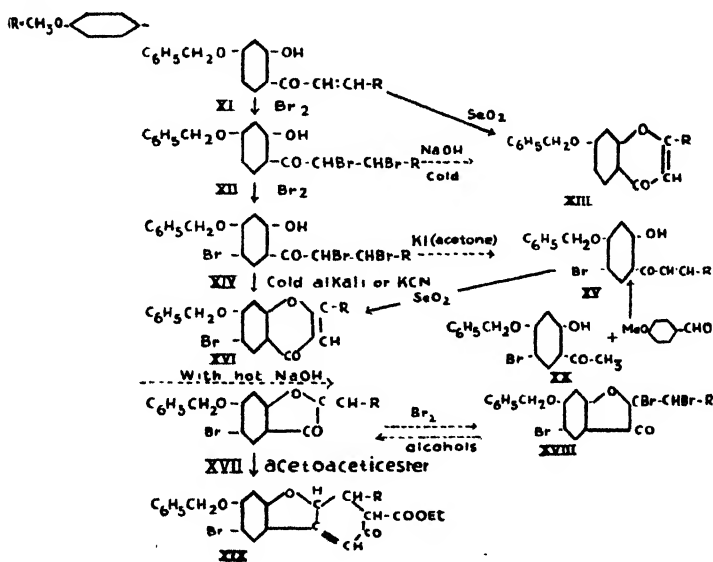


2 : 4-dimethoxyphenyl-6'-bromo-3' : 4'-methylenedioxystryryl ketone.—(I; see fig. 1) formed on synthesis two isomers which gave the same dibromide (not isolated); this behaviour in chalcones has been investigated by Weygand in a series of papers (see, *e.g.*, Ber., 1929, 62, 2603). Further bromination results in a bromine atom entering the dimethoxyphenyl nucleus in the 5 position as shown at (IV), since the chalcone (V) obtained from bromide (IV) by the action of potassium iodide was also obtained from bromodimethylresacetophenone

(J. Amer. Chem. Soc., 1919, 41, 262) and 6-bromo-piperonal. The position assigned to the bromine atom in bromodimethylresacetophenone is based on the fact that 2:4-dimethoxy-benzoic acid gives the 5-bromoderivative (see Rice, J. Amer. Chem. Soc., 1926, 48, 3125); further Auwers and Pohl (Ann., 1914, 405, 274) found that chlorine entered the 5-position in 2-hydroxy-4-methoxy- ω -chloracetophenone. Both the isomers of the chalkone (I) gave the same *phenylhydrazone* of 2:4-dimethoxyl phenyl 6'-bromo-3':4'-methylenedioxy-styryl ketone (II) which did not give Knorr's pyrazoline colour reaction and dissolved slowly in concentrated sulphuric acid with the formation of colour; also the two isomers yielded the same ethyl-2-(6'-bromo-3':4'-methylenedioxyphenyl)-4-(2₁:4₁-dimethoxyphenyl)- Δ^4 -cyclohexene-6-one-I-carboxylate (III) with acetoacetic ester.

The chalkone (I) on treatment with hydriodic acid was demethylated to give 2-hydroxy-4-methoxyphenyl-6'-bromo-3':4'-methylenedioxy-styryl ketone (VI) which was also obtained from 4-methylresacetophenone and 6-bromopiperonal; the *acetoxy-chalkone dibromide* (VIII) with hot alkali gave the *benzylidene-coumaranone* (IX) which gave deep red colour with concentrated sulphuric acid. Chalkone (VI) condensed with acetoacetic ester to yield Ethyl-2-(6'-bromo-3':4'-methylene-dioxyphenyl)-4-(2₁-hydroxy-4₁-methoxyphenyl)- Δ^4 -cyclohexene-6-one-I-carboxylate (X).

Fig. 2



Similar experiments were carried out with benzyloxy-chalkone (XI; see fig. 2). The *dibromide* (XII) with cold alkali gave a flavone (XIII) which has been previously obtained by the direct oxidation of (XI) with selenium dioxide (*cf.* Mahal, Rai and Venkatraman, J. C. S. 1935, 106, 866). Further bromination resulted in bromine atom entering the dihydroxy phenyl nucleus. *Tribromide* (XIV) gave a *flavone* (XVI) or *benzylidenecoumaranone* (XVII) according to the reagent used (see, *e.g.*, Wheeler and Collaborators, Proc. National Institute of Sciences of India, Vol. V, No. 2, 267). The flavone (XVI) was also obtained by the direct oxidation of chalkone (XV) with selenium dioxide. The coumaranone (XVII) with bromine (1 mol.) yielded a *dibromide* (XVIII) (*cf.* Rao and Wheeler, J. C. S., 1939, 110, 1004) which on boiling with ethyl or methyl alcohol gave back the coumaranone, unlike some of the chalkone dibromides (Wheeler and Collaborators, loc. cit.) where only one of the bromine atoms is labile. It is observed that both the bromine atoms in the coumaranone dibromide are labile. The keto-ethylene group in (XVII) reacts with ethyl acetoacetate like the same group in a chalkone to give a *substance* which has probably formula (XIX; *cf.* Panse and Wheeler, Current Science, 1938, 7, 181; and also Rao and Wheeler, loc. cit.) which is based on the course of the well-known Knoevenagel condensation of chalkones with ethyl acetoacetate (Annalen, 1894, 281, 58). The position of the nuclear bromine atom in the chalkone bromide (XIV) is based on the considerations outlined above. The bromine is not in the benzyl nucleus since the chalkone (XV) obtained by the action of potassium iodide on (XIV) was also obtained from bromobenzylresacetophenone (XX) and anisaldehyde.

EXPERIMENTAL

2 : 4-dimethoxyphenyl-6'-bromo-3':4'-methylenedioxy-styryl ketone (I).—A mixture of 2:4-dimethylresacetophenone (22 g.) (Perkin, Robinson and Turner, J. C. S., 1908, 93, 1108) and 6-bromopiperonal (28 g.) (Ber., 1891, 24, 2491) in alcohol (250 ccs.) was treated with aqueous sodium hydroxide (20%; 30 ccs.) and heated under reflux for 5-10 minutes at 100°C when the chalkone separated in fine yellow crystals (3½ g.).

1. Isomer : The separated chalkone (I) crystallised from alcohol-ethyl acetate in microscopic yellow needles, m.p. 147-48°: (Found : Br, 20.3 ; $C_{18}H_{15}O_5$, Br requires Br, 20.5%).

2. Isomer: The same chalkone (1) crystallised from glacial acetic acid-alcohol in white large needles, m.p. 137-38°. If the molten sample of the white variety in the capillary tube (while noting down the melting point) is allowed to resolidify, the melting point rises to 147-48°. There is no depression in the mixed melting point which lies in between the two.

Phenyl-hydrazone of 2:4-dimethoxyphenyl-6'-bromo-3':4'-methylenedioxystyryl ketone (II).—2:4-dimethoxyphenyl-6'-bromo-3':4'-methylenedioxystyryl ketone (I; 1 or 2 isomer, 2 g.) in glacial acetic acid (20 ccs.) was treated with phenylhydrazine (3 ccs.), and the mixture heated for 30 minutes at 100°, the whole was diluted and acidified with hydrochloric acid. The product (3 g.) crystallised from ethyl acetate, in white needles, m.p. 168-69°. It gives greenish blue fluorescence in ethyl acetate, glacial acetic acid, etc. (Found: Br, 17.2; $C_{24}H_{21}O_4$ Br requires Br, 16.7%). The substance dissolved slowly in conc. sulphuric acid with the formation of colour; and the resulting solution did not give a colour with ferric chloride.

Ethyl-2-(6'-bromo-3':4'-methylenedioxyphenyl)-4-(2:4-dimethoxyphenyl)- Δ^4 -cyclohexene-6-one-I-carboxylate (III).—A mixture of sodium ethylate (0.8 g. in 25 ccs. abs. alcohol), acetoacetic ester (5 g.), 2:4-dimethoxyphenyl-6'-bromo-3':4'-methylenedioxystyryl ketone (I; 6 g.) and alcohol (80 ccs.) was heated under reflux at 80-90° for 2 hours, diluted and acidified with hydrochloric acid. The resulting pasty mass solidified on keeping in contact with petrol for 2 days. The product (3 g.) crystallised from a mixture of alcohol ethyl acetate in microscopic needles, m.p. 152-53°. (Found: Br, 15.5; $C_{24}H_{23}O_7$ Br requires Br, 15.9%).

2:4-dimethoxy-5-bromophenyl- α - β -dibromo- β -6'-bromo-3':4'-methylenedioxyphenylethyl-ketone (IV).—Either of the two isomers of chalkone (1:7.8 g.) in a mixture of chloroform-carbon; tetrachloride was treated with bromine (2 mols; 6.4 g.), when (IV) separated in white crystals. The product (8 g.) crystallised from benzene in white microscopic soft needles, m.p. 188-89°. (Found*: Br, 50.8; $C_{18}H_{14}O_5$ Br₄ requires Br, 50.8%).

2:4-dimethoxy-5-bromophenyl 6'-bromo-3':4'-methylenedioxystyryl ketone (V).—The preceding bromide (IV; 1 g.) in hot acetone was heated under reflux for 10 minutes at 90-100° with potassium iodide dissolved in a small quantity of water and

acetone, when iodine was liberated. The product (4 g.) separated immediately and crystallised from nitrobenzene in pale yellow needles, m.p. 257-58°. (Found* : Br, 33.8; $C_{18}H_{14}O_8$ Br₂ requires Br, 34.1%). It was also formed when a mixture of 6-bromopiperonal (4.6 g.), alcohol (150 ccs.), 6-bromo-3:4-dimethylresacetophenone (5.2 g.), and aqueous sodium hydroxide (20% ; 4 ccs.) was heated under reflux at 90-100° for one hour. The chalkone (5 g.) separated and crystallised from nitrobenzene-toluene.

2-hydroxy-4-methoxyphenyl-6'-bromo-3' : 4'-methylenedioxy-styryl ketone (VI).—To a solution of chalkone (1; 2 g.) was added slowly a mixture of hydriodic acid (20 ccs.) and acetic anhydride (10 ccs.) which were mixed up previously by cooling, as the action of hydriodic acid with acetic anhydride is very reactive. The reaction is vigorous with great evolution of heat and the mixture is to be added under strong cooling and the process takes about 15-20 minutes. A dirty brown solid separated which crystallised from alcohol-ethyl acetate in shining orange yellow needles, m.p. 210-11°. (Found : Br, 20.9; $C_{17}H_{13}O_5$ Br requires Br, 21.2%). It was also prepared when a mixture of 4-methylresacetophenone (1.8 g.) (Adams, J. Amer. Chem. Soc., 1919, 41, 260), 6-bromopiperonal (2.3 g.), alcohol (50 ccs.) and aqueous sodium hydroxide (20% ; 2 ccs.) was kept for 12 hours. The chalkone (2.5 g.) separated and crystallised from alcohol-ethyl acetate in yellow needles.

2-acetoxy-4-methoxyphenyl-6'-bromo-3' : 4'-methylenedioxy-styryl ketone (VII).—A mixture of the preceding chalkone (VI; 7 g.), acetic anhydride (20 ccs.) and pyridene (7 ccs.) was boiled for one hour and kept for 12 hours. The solution was diluted and the product (7 g.) crystallised from alcohol-ethyl acetate in pale yellow needles, m.p. 158-59°. (Found : Br, 19.2; $C_{19}H_{15}O_6$ Br, requires Br, 19.1%).

2-acetoxy-4-methoxyphenyl- $\alpha\beta$ -dibromo- β -6'-bromo-3' : 4'-methylenedioxyphenyl-ethyl ketone (VIII).—The acetyl derivative (VII; 21 g.) in chloroform (150 ccs.) was treated with bromine (8 g.) in carbon tetrachloride (50 ccs.). The product (20 g.) separated and crystallised from benzene in white needles, m.p. 194-195°. (Found : Br, 41.9; $C_{19}H_{15}O_6$ Br₂ requires Br, 41.5%). Chalkone (VI) was obtained when the bromide (VIII) was treated with potassium iodide in hot acetone.

3:4-methylenedioxy-6-bromobenzylidene-6'-methoxycoumaranone (IX).—The preceding bromide (VIII; 2 g.) in hot

alcohol (50 ccs.) was treated with aqueous sodium hydroxide (20%; 2 ccs.) and the mixture was heated under reflux for 10 minutes at 80–90°. The resulting orange coloured solution was diluted and acidified with hydrochloric acid when yellow precipitate (1 g.) separated. It crystallised from alcohol in yellow needles, m.p. 224–225°. (Found: Br, 21.7; $C_{17}H_{11}O_5Br$ requires Br, 21.3%). It forms red solution with conc. sulphuric acid.

Ethyl-2-(6'-bromo-3':4'-methylenedioxyphenyl)-4-(2,1-hydroxy-4,1-methoxy phenyl)- Δ^4 -cyclohexene-6-one-1-carboxylate (X).—A mixture of sodium ethylate (0.4 g. in 10 ccs. abs. alcohol), ethyl acetoacetate (2 ccs.), 2-hydroxy-4-methoxyphenyl-6'-bromo-3':4'-methylenedioxyethyl ketone (VI; 2 g.) and alcohol (25 ccs.) was heated under reflux at 80–90° for 2 hours, the whole was diluted and acidified with hydrochloric acid. The paste solidified on keeping in contact with petrol for 24 hours. The product (2 g.) crystallised from alcohol ethyl-acetate in white needles, m.p. 215–16°. (Found: Br, 16.4; $C_{25}H_{21}O_7Br$ requires Br, 16.3%).

2-hydroxy-4-benzyloxy phenyl- $\alpha\beta$ -dibromo- β -4'-methoxyphenylethyl-ketone (XII).—To a suspension of 2-hydroxy-4-benzyloxyphenyl-4'-methoxy-styryl ketone (XI; 4.5 g.) in benzene (100 ccs.) was added bromine (2 g.) and the mixture was thoroughly shaken. The benzene solution was diluted with petroleum benzine when the bromide separated in the form of pale yellow fine powder (4.5 g.). It crystallised from benzene-benzine in fine white needles, m.p. 150–51°. (Found: Br, 31.2; $C_{25}H_{20}O_4Br_2$ requires Br, 30.8%). Three crystallisations were required to obtain pure product.

7-benzyloxy-4'-methoxyflavone (XIII).—To a suspension of the preceding bromide (XII; 2 g.) in alcohol (30 ccs.) was added aqueous sodium hydroxide (40%; 5 ccs.) and the mixture shaken. Yellow precipitate (1 g.) separated from the orange yellow coloured solution. It crystallised from alcohol in yellow needles, m.p. 136–37°. The substance has previously been prepared (m.p. 137°) by Mahal, Rai and Venkartaman (See J. C. S., 1935, 160, 866) by oxidation of the chalkone (XI) with selenium dioxide with which it did not give depression in the mixed melting point.

2-hydroxy - 4 - benzyloxy - 5-bromophenyl- $\alpha\beta$ -dibromo- β -4'-methoxyphenylethyl ketone (XIV).—was prepared by the action of bromine (2 mols.) on (XI) in a mixture of chloroform-carbon-

tetrachloride. It crystallised from benzene-petrol in white wooly needles, m.p. 166-67°. (Found: Br, 40.4; $C_{23}H_{19}O_4Br_2$ requires Br, 40%).

2-hydroxy-4-benzyloxyphenyl-4'-methoxystyryl ketone (XV).—The preceding bromide (XIV) in hot acetone was treated with potassium iodide as in (V). It crystallised from alcohol-acetone in yellow needles, m.p. 153-54°. (Found: Br, 18.4; $C_{23}H_{19}O_4Br$ requires Br, 18.2 %). The chalkone was also formed when a mixture of 6-bromo-4-benzylresacetophenone (XX; 3.2 g.), alcohol (100 ccs.), anisaldehyde (1.4 g.) and aqueous sodium hydroxide (20 %; 5 ccs.) was heated under reflux at 90-100° for 15 minutes and kept for 24 hours. On dilution a paste separated which solidified on keeping in contact with petrol. It crystallised from alcohol-ethyl acetate in yellow needles.

6-bromo-7-benzyloxy-4'-methoxyflavone (XVI).—(XIV) in acetone was treated with aqueous sodium hydroxide (20 %) and the mixture thoroughly shaken. The yellow precipitate crystallised from a mixture of methyl alcohol-benzene in pale yellow needles, m.p. 200-1°. (Found: Br, 18.5; $C_{23}H_{17}O_4Br$ requires Br, 18.4 %). It gives skyblue fluorescence with sulphuric acid and glacial acetic acid. It was also prepared by using alcoholic potassium cyanide in place of aqueous sodium hydroxide. The same flavone has also been obtained by the oxidation of (XV) with selenium dioxide as in the case of (XIII).

Oxidation of the chalkone (XV).—A mixture of (XV; 2.5 g.), selenium dioxide (3g.) and amyl alcohol (30 ccs.) was heated at 150° under reflux for 5 hours. After the black precipitate of selenium was removed by filtration, flavone (2g.) separated. There was no depression in the mixed m.p. with (XVI).

4-methoxybenzylidene-5'-bromo-6'-benzyloxy coumaranone (XVII).—(XIV; 2g.) in methyl alcohol (25 ccs.) was treated with aqueous sodium carbonate (20 %; 2 ccs.) and the mixture was boiled for an hour. The resulting yellow solution was diluted and acidified with hydrochloric acid. The yellow precipitate (1 g.) crystallised from alcohol-benzene in yellow needles, m.p. 209-10°. (Found: Br, 18.8; $C_{23}H_{17}O_4Br$ requires Br, 18.4 %). It gives red colour with concentrated sulphuric acid.

Dibromide of 4-methoxybenzylidene-5'-bromo-6'-benzyloxy coumaranone (XVIII).—The preceding coumaranone (XVII; 2.2 g.) in chloroform (50 ccs.) was treated with bromine (0.8 g.) and the mixture heated at 90-100° for 30 minutes. On diluting

the solution with petrol, white precipitate (2 g.) separated; it crystallised from chloroform carbon tetrachloride in pale yellow needles, m.p. 170-71°. (Found: Br, 40.2; $C_{23}H_{17}O_4Br_3$ requires Br, 40.2%). Compound (XVII) was obtained back when (XVIII) was boiled with methyl or ethyl alcohol for two hours.

Condensation of ethyl acetoacetate with 4-methoxybenzylidene-5'-bromo-6'-benzyloxy coumaranone (XIX).—A mixture of coumaranone (XVII; 1 g.) in alcohol (100 ccs.) sodium ethylate (0.6 g. in 25 ccs. abs. alcohol) and ethyl acetoacetate (4 ccs.) was heated under reflux at 90-100° for 4 hours, the whole was diluted and acidified with hydrochloric acid. The product (0.5 g.) crystallised from acetone-alcohol in white needles, m.p. 205-6°. (Found: Br, 14.9; $C_{29}H_{25}O_6$ Br requires Br, 14.6%).

2-hydroxy-4-benzyloxy-5-bromo-acetophenone (XX).—2-hydroxy-4-benzyloxyacetophenone (2.4 g.) in carbon disulphide (50 ccs.) was treated with bromine (1.6 g.) in presence of a crystal of iodine as a catalyst. Excess of carbon disulphide was distilled off, and the white crystalline product (3 g.) crystallised from alcohol-ethyl acetate in white needles, m.p. 154-55°. (Found: Br, 25.6; $C_{15}H_{13}O_3$ Br requires Br, 25.2 %).

Analyses of the compounds marked (*) were carried out by the Chemical Analyst at the Royal Institute of Science, Bombay.

The author expresses his grateful thanks to Dr. T. S. Wheeler for his keen interest and valuable guidance during the course of this work and to the University of Bombay for a grant which has partially helped the investigation.

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BIOCHEMICAL STUDIES IN THE GROWTH AND RIPENING OF A BANANA

By

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INTRODUCTION

THE banana is one of the most popular fruits in India and enjoys a very wide trade. Its cultivation is supposed to date back even to pre-historic ages. The earliest Greek, Latin and Arab records have referred to it as a remarkable Indian fruit. Its diffusion to other countries is believed to be contemporaneous with or even anterior to that of the human races. The seedless banana of to-day is the result of long cultivation with conscious selection of superior types.

There are a large number of varieties of banana spread all over India. Most of them are localised and their cultivation is limited to the regional market demands. More recently, the fruit has developed an export trade particularly from the West Indies. In this connection, a large amount of systematic work has been published in the methods of cultivation, transportation and storage of this fruit.

A certain amount of work has been recorded in literature on the changes taking place during the ripening of the banana fruit. Gore (Jour. Agri. Res., 1914, 3, 187) has extensively reviewed the work on the physiology of the banana. He himself has investigated the process of ripening of the banana in detail. According to him, the saccharification of starch is the main chemical change during ripening. The moisture content of the pulp increases with the progress of saccharification. This incoming water is traced to its loss in the peel. Stratten and his co-workers (Plant Physiol., 1931, 6, 361) have confirmed this finding by a study of the osmotic pressure relationships between pulp and peel during ripening.

Analyses of the ripe fruits of the various local varieties have been published from different centres both in India and

abroad. Among other works on banana may be mentioned that of Sastri, *et. al.* (Proc. Indian Acad. Sci., 1934, 6, 318) on its amylase and Rangathan (Jour. Indian Inst. Sci., 1928, XI A, 80) on its tannin.

Most of the work on ripening reviewed refers only to the changes in the mature fruit. Further, the fruit employed by the European and American workers was brought from distant places under controlled conditions of storage which are well known to modify the natural processes of ripening. In the present work, fruits fresh from the field have been employed and changes from the very early to the post-ripening stages have been investigated. As is well known, these changes are very gradual up to the stage of maturity of the fruit but are very rapid during the short interval of ripening of the mature fruit after harvesting. These two stages have been separately investigated for changes in the physical and chemical constituents and also in the respiratory and catalase activities.

MATERIAL AND METHODS

There are five varieties of banana usually found in the Poona market. Their analysis is given in Table 1. Of these, only two varieties, the *Basrai* and the *Rajapuri*, were employed in this investigation. The *Basrai* is the most popular variety in the Poona market. It has the best average composition, is fairly large in size and has a mild flavour and an agreeable taste. It is also

TABLE 1

Composition of the pulp of the different varieties of banana
(Expressed as percentage of fresh weight of pulp)

Variety	Average weight of fruit	Pulp: Peel ratio	Dry matter	Nitrogen	Acidity (as gms. of KOH)	Total sugars	Reducing sugars	Non-reducing sugars	Alcohol insoluble matter	Vitamin C*
<i>Welchi</i> ...	75.06	3.30	29.41	0.183	0.579	20.17	19.20	0.97	6.09	5.33
<i>Rajapuri</i>	69.09	1.80	30.28	0.170	0.547	21.84	21.39	0.45	5.56	...
<i>Junnar</i>	121.16	2.39	22.34	0.189	0.519	16.77	11.67	5.10	2.54	2.41
<i>Basrai</i> ...	178.57	2.61	27.04	0.156	0.347	18.61	16.28	2.33	5.15	3.91
<i>Soni</i> ...	63.48	2.66	31.26	0.202	0.527	21.47	16.78	4.69	6.16	1.54

As mgs. per 100 gms. of the pulp.

the most suitable for transportation owing to its big size and stiff peel. The *Rajapuri* variety is a smaller fruit with a better flavour and more attractive colour. Both the varieties of fruits were obtained from the Fruit Experiment Station, Kirkee, through the kind courtesy of the Horticulturist to the Government of Bombay. The requisite number of bearing plants were labelled and numbered. The age of each bunch was calculated from the date of appearance of the hand containing sterile flowers. Samples were removed at intervals of fifteen days. Each sample consisted of a complete bunch containing about twelve to fifteen hands and each hand contained ten to twelve fruits.

The hands on a banana bunch are exposed gradually from above downwards. It is possible, therefore, that the age of each hand of a bunch slightly decreases from top to bottom. Chemical analysis of upper, middle and lower hands showed a slight variation in composition. The fruits at the top are bigger and those at the bottom smaller than the average middle fruits. Therefore, for sampling purposes, the first two and the last two hands were discarded and the fruits on the hands in the middle of a bunch were randomised. The distribution of pulp in the fruit is not uniform in all stages of growth. It is more concentrated in the middle than in the narrowing ends. The distribution in the middle, however, is more uniform throughout the growth. Hence the fruits were cut into four equal parts and only the two middle parts employed for further analysis. For physical measurements ten fruits were taken at random from the bunch and for chemical analysis ten to twenty fruits were taken from the randomised lot. Peel and pulp were separated by means of a sharp knife, cut into thin pieces and separately analysed for the various constituents.

The length, circumference, volume, weight and quantity of pulp and peel of each fruit were determined immediately after the sampling. Chemically, the pulp and peel were analysed separately for dry matter, astringency, acidity, carbohydrates, nitrogen, ash and ash constituents.

Dry matter.—Preliminary trials were made to find out a suitable method to determine dry matter, by drying the pulp only, pulp treated with alcohol and pulp treated with alcohol and calcium carbonate. These were placed on the top of a water oven for four hours and then transferred inside the oven where the temperature was 98°C. and hourly loss of weight was recorded (Table 2).

TABLE 2

Rate of loss of moisture during drying of banana pulp under different treatments.

(Expressed in per cent. of fresh weight)

Hours	Pulp alone	Pulp plus alcohol	Pulp plus alcohol plus calcium carbonate
1	63.76	69.96	...
2	6.70	1.17	...
3	0.98	1.09	70.53
4	1.40	0.13	1.20
5	0.42	0.18	0.40
6	0.21	0.06	0.06
7	0.10	0.06	0.03
8	0.31	...	0.04

It can be seen that the material is continuously losing weight. But the rate of loss of moisture after the first five hours is least in the last treatment. According to Archibold (Ann. Bot., 1928, 42, 541), this continued loss is due to the decomposition of sugars and this is effectively reduced to a minimum by the treatment. Moreover, the untreated sample showed distinct signs of caramelisation. Therefore, for determining dry matter, the fresh material was treated with calcium carbonate and 95 per cent. alcohol and dried for four hours on a water oven and one hour inside it. During drying, 95 per cent. alcohol was twice added.

Carbohydrates.—Fresh material was soaked in enough alcohol to give a final concentration of 80 per cent. by volume and then extracted in a Soxhlet with 80 per cent. alcohol for 12 hours. The alcohol was evaporated off, the extract clarified by neutral lead acetate and sodium phosphate and the sugars estimated by Bertrand's method. Starch was estimated in the residue by the taka-diastase method. The residue from this was hydrolysed with 2.5 per cent. hydrochloric acid for 2.5 hours, and the sugars estimated in the hydrolysate. This is the acid-hydrolysable matter and is expressed in terms of glucose. The figures represent the amount of easily hydrolysable cell-wall incrustations such as the pectins and hemicelluloses.

Astringency.—Preliminary trials for extracting the tannins with water, alcohol, ethyl acetate and acetone showed acetone to be the most efficient extractant. Fresh material was steeped in acetone and later extracted in a Soxhlet till the sample gave no blue colouration with ferric chloride. The astringency of the extract was estimated by the permanganate method of Lowenthal with the modification of Monier and Proctor as described in Allen's Commercial Organic Analysis, Edition 3, Volume 5. The results are expressed in terms of oxalic acid.

Ash.—Amongst the various ash constituents magnesia, lime and phosphoric acid were estimated volumetrically (Wright's Soil Analysis, 1934), potassium by the volumetric method of Milne (Jour. Agri. Sci., 1929, 19, 547), iron by the thiocyanate method given by Farrar Jr. (Jour. Biol. Chem., 1935, 110, 685) and copper by the diethyl-dithio-carbamate method as modified by Hoar (Analyst, 1937, 62, 657).

Respiration.—The respiratory activity of the fruits was studied by the flow method using an apparatus similar to that of Harding and others (Science, 1929, 70, 125) with slight modi-

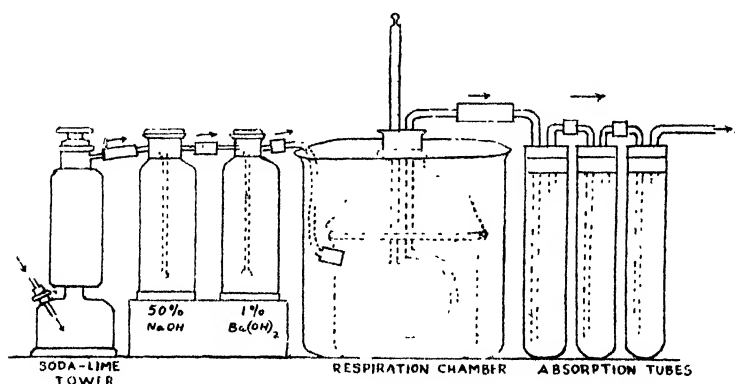


FIG. 1. Respiration Apparatus

fications (Fig. 1). Three to six fruits were weighed and placed in the respiration chamber, CO₂-free air was drawn through the apparatus at the rate of 1500 ml. per hour for two hours, and the carbon dioxide respired was estimated by absorbing it in 0.2N bariumhydroxide. For each batch of fruits the average of two consecutive readings, each of two hours duration was taken. The results are expressed as mg. of carbon-dioxide respired per hour per kilo of fruit.

While titrating the barium hydroxide solution with 0.1 N oxalic acid in the presence of barium carbonate, the end point is

very indistinct when phenolphthalein is used as indicator. To obviate this difficulty, Treadwell and Hall recommend the use of turmeric paper as an external indicator. Even this did not give accurate results owing to the inherent defects of an external indicator. After a number of trials, it was found that it was possible to get sharp and definite end points even with phenolphthalein, by adding just before titration, 10 to 15 mls. of 25 per cent. barium chloride solution. The excess of barium ions may perhaps have suppressed the hydrolysis of barium carbonate and barium oxalate, both slightly soluble.

Catalase activity.—The gasometric method was employed. A sketch of the apparatus is given in Fig. 2. A weighed quantity

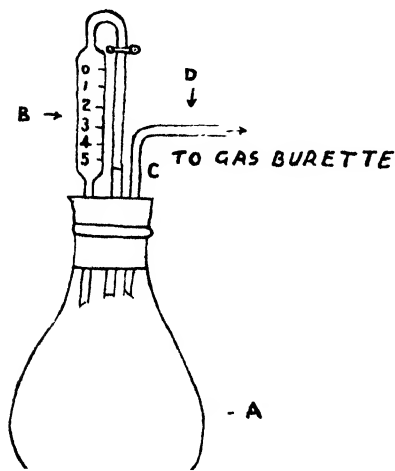


FIG. 2. Catalase Apparatus

of the material prepared according to Harding (Jour. Agri., Res., 1936, 53, 43) was placed in the 100 ml. conical flask. The graduated pipette was filled with hydrogen peroxide, and connected to the flask as shown in figure. This arrangement prevented any change in volume when the hydrogen peroxide was let in by opening the pinchcock, after connecting the apparatus to the gas burette. The flask was kept in a water bath at room temperature, shaken for exactly five minutes and the volume of air displaced into the gas burette was read off at atmospheric pressure. The results are expressed as mls. of oxygen per gram for five minutes.

RESULTS AND DISCUSSION

The banana takes about 120 days to mature on the plant. Thereafter the bunches are harvested and ripened by storing in a warm place. As already stated, these two aspects—the growth up to maturity and the ripening—have been separately studied. The *Basrai* banana was used for the former and the *Rajapuri* for the latter study.

CHANGES DURING GROWTH

Physical changes.—THE physical changes in *Basrai* fruits up to maturity are given in Table 3.

TABLE 3

Physical changes in the *Basrai* banana during growth

Age in days	Length	Maximum circumference	Volume	Fresh weight per fruit	Rate of increase of weight per day	Dry matter per fruit	Rate of increase dry matter per day	Weight of pulp per fruit	Weight of peel per fruit
	cm.	cm.	c. c.	gm.	gm.	gm.	gm.	gm.	gm.
0	10.97	7.44	30.4	25.25	...	2.24	...	7.59	17.66
15	11.72	7.91	38.4	33.29	0.54	3.71	0.098	13.36	19.93
30	10.46	8.26	42.5	35.78	0.17	5.10	0.093	17.52	18.24
45	11.21	8.60	45.4	43.33	0.53	7.45	0.156	23.36	19.97
60	11.58	9.80	64.1	61.29	1.00	11.20	0.210	34.64	26.65
75	12.06	9.90	71.5	65.84	0.38	13.11	0.159	37.82	28.02
90	71.34	0.29	14.85	0.091	44.9	26.44
105	12.20	10.90	82.0	78.64
120	78.00	...	13.96	0.03	46.49	31.51

The length of the fruit does not show any marked increase during the period under observation. The maximum circumference of the fruit is constantly increasing throughout the growth though at a very gradual rate. But the volume of the fruit shows a rapid increase from the very beginning (Fig. 3). The increase

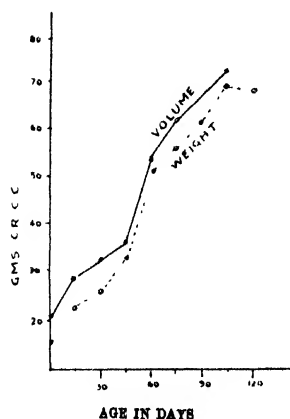


FIG. 3. Volume and Weight Changes in Fruit

in volume is very quick between the 45th and 60th days. Though the length and circumference increase very slowly, the volume increases at a very rapid rate. This can be explained as being due to the filling of the extremities of the fruit and the rounding of the corners. The graphs for fresh weight and volume of the fruit (Fig. 3) are very similar. These curves possess the characteristic sigmoid form. Gustaffson (Plant. Physiol., 1926, 1, 265; 1929, 4, 349) has reported similar findings in the case of tomatoes,

oranges and other fruits. Thus, the nature of fruits may vary, but the process of growth in all cases can be expressed by an auto-catalytic expression. During the last fortnight before harvesting, the fruit, even though on the plant, shows no increase in fresh weight. Archibold (Ann. Bot., 1932, 46, 407) and Singh (Indian Jour. Agri. Sci., 1937, 7, 176) have observed similar cessation of growth indicating maturity in the fruits they studied.

The rates of increase of fresh weight and of dry matter per day per fruit are shown graphically in Fig. 4. The two curves are

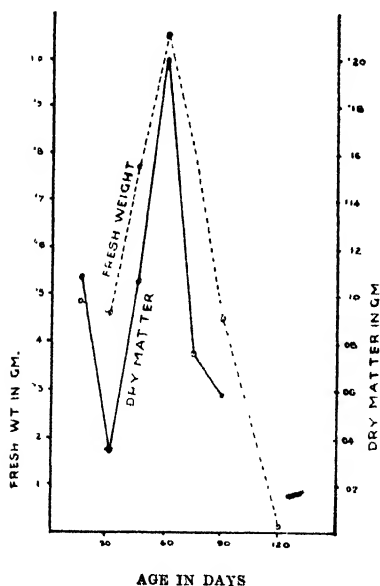


FIG. 4. Rates of Increase of Fresh Weight and of Dry Matter Per Fruit Per Day

very similar. The nature of these curves divides the life of the banana fruit into three distinct stages. The first one of 30 days when the growth rate is falling, the second one of another 30 days when the growth rate suddenly rises and reaches a maximum and the last one of the remaining 60 days during which the growth rate sharply declines to zero. During the second half of the last stage there is a cessation of growth with no increase either in fresh weight or dry matter.

The initial fall in the growth rate as found in the banana has not been observed in apples (Archibold, Ann. Bot., 1928, 42, 541), nor in mangoes and guavas (Singh, *loc. cit.*). In these fruits, the growth rate as measured by the increase of dry matter, increases right from the start. An initial fall in growth rate has, however, been observed by Singh (*loc. cit.*) in the case of the Krishnabagh variety of mangoes only.

The ratios of the rate of increase of dry matter to the rate of increase in fresh weight are plotted in Fig. 5. They show an inverse relation to the growth rate, as measured either by fresh weight or by dry matter of the fruit. This ratio is proportional to the concentration of the solids in the fruit sap. Its inverse relation to growth rate suggests that the growth rate is high when the sap concentration is low. The high rate of increase of dry matter during this period seems

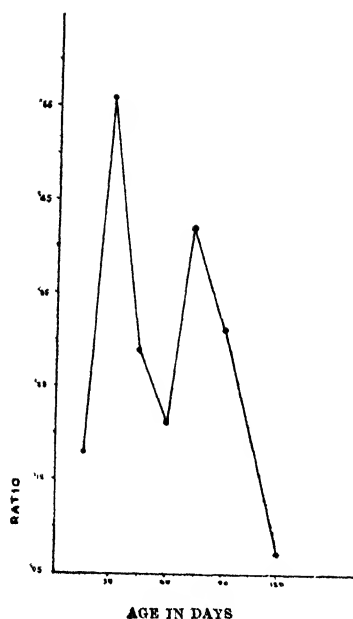


FIG. 5. Ratio of Rate of Increase of Dry Matter to that of Fresh Weight

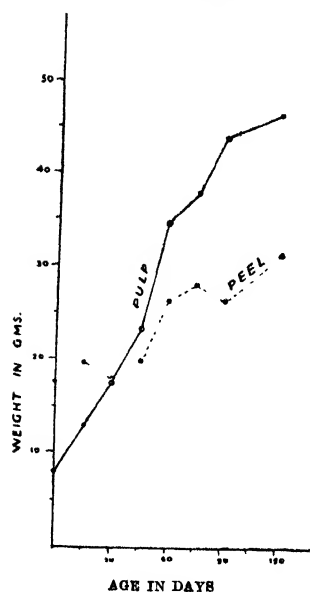


FIG. 6. Fresh Weights of Pulp and Peel per Fruit

to indicate a rapid diffusion of sap into the fruit which may perhaps be due to its low viscosity.

The thick peel of the banana contributes considerably to the total weight of the fruit. It forms the major part of the fruit during the early stages (Table 3 and Fig. 6). The weight of peel is greater than that of pulp during the first month. By the end of the first month, the weight of pulp increases and becomes equal to that of peel. Thereafter both increase at an equal rate till the end of the second month. After this the pulp continues to increase at the same rate while the peel slows down considerably.

Chemical changes.—The chemical analysis of the pulp and peel of the *Basrai* banana at the different stages of growth are given in Tables 4 and 5. In Table 6 is shown the distribution of starch and nitrogen between pulp and peel per fruit.

The main activity during the growth of the fruit seems to be centred round the synthesis and accumulation of starch in the pulp. Starch is present from the very beginning and rapidly accumulates till the 75th day when it is at its maximum. At this point, the starch represents nearly 80 per cent. of the total dry matter of pulp. The starch curve very closely follows the dry matter curve (Fig. 7). At the peak point the starch content of pulp is about 9 grams per fruit (Table 6). After the fruits are removed

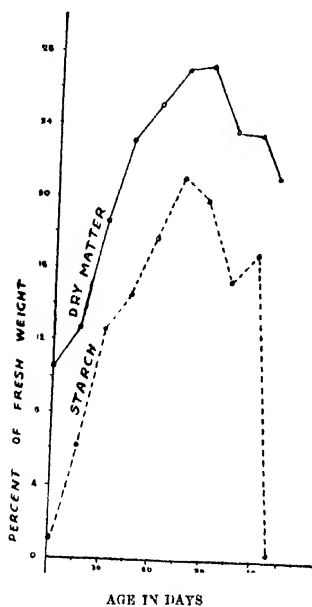


FIG. 7. Dry Matter and Starch in Pulp

from the plant for ripening almost the whole of the starch is converted into sugars during the short period of about 10 days.

The peel stores but little starch and here also the changes in starch content are very similar to those in the pulp. As before, the maximum is reached on the 75th day and after the removal of the fruit from the plant almost the whole of the starch of the peel is converted into sugars. At the maximum, the starch content of peel is only about 1 gram per fruit which represents about 35 per cent. of the total dry matter.

The distribution of nitrogen in pulp and peel per fruit (Table 6) is unequal. In the early stages the nitrogen content of peel per fruit is more than that of pulp. But the total peel nitrogen remains more or less constant during growth while the

pulp nitrogen increases steadily right from the beginning.

TABLE 4

Chemical composition of the *Basrai* banana *pulp* at different stages of growth
(Expressed as percentage of fresh weight of pulp at the time of sampling)

Age in days	Dry matter	Nitrogen	Starch	Acid hydro- lysable matter	*Residue	Reducing sugars	Non-reducing sugars	Total astrin- gency	Acidity as gms. KOH
0	10.53	0.17	0.75	2.25	5.23	T	T	0.04	...
15	12.62	0.15	6.16	0.96	4.47	r	r	0.03	0.08
30	18.59	0.19	12.58	0.86	3.86	a	a	0.24	0.06
45	23.31	0.23	14.56	1.14	4.58	o	o	0.30	0.03
60	25.11	0.23	17.75	0.94	4.91	e	e	0.15	0.08
75	27.15	0.21	21.10	0.92	4.43	s	s	0.07	0.06
90	27.33	0.20	19.98	0.58	5.13	0.12	0.43	0.04	0.08
105	23.66	0.27	15.48	0.66	3.71	0.07	0.02	0.02	0.18
120†	23.65	0.15	16.93	0.69	4.27	0.06	0.16	0.01	0.20
126	29.18	...	1.11	0.23	6.89	0.14	0.14	...	0.50
130	21.20	...	0.47	0.26	1.93	11.66	1.88	...	0.25

* Alcohol insoluble matter minus starch and acid hydrolysable matter.

† The bunch was removed from the plant at this stage and kept for ripening.

TABLE 5

Chemical composition of the *Basrai* banana peel
at different stages of growth

(Expressed as percentage of the fresh weight of peel at
the time of sampling)

Age in days	Dry matter	Nitrogen	Starch	Acid hydro- lysable matter	Residue*	Reducing sugars	Non-reducing sugars	Total astring- ency	Acidity as gms. KOH
0	8.14	0.16	0.43	2.35	3.65	T r e e s	T r e e s	0.04	..
15	10.17	0.13	2.07	1.14	4.42			0.02	0.05
30	10.12	0.13	4.57	1.15	2.97			0.07	0.11
45	10.01	0.16	2.78	1.34	4.23	0.10	...	0.03	0.05
60	9.40	0.11	2.83	1.24	3.31	0.11	0.20	0.06	0.07
75	10.15	0.12	3.56	1.37	3.77	0.06	0.02	0.18	0.04
90	9.71	0.12	2.70	1.26	3.51	0.07	0.14	0.12	0.04
105	7.35	0.13	2.37	0.99	1.90	0.06	0.13	0.36	0.08
120†	9.42	0.10	2.30	1.18	3.46	0.08	0.13	0.16	0.06
126	14.63	...	1.16	1.77	6.32	0.93	2.09	...	0.12
130	14.27	...	0.43	1.28	5.00	3.77	0.94	...	0.08

* Alcohol insoluble matter minus starch and acid hydrolysable matter.

† The bunch is removed from the plant and kept for ripening.

TABLE 6

Distribution of starch and nitrogen between pulp and peel
per fruit of the *Basrai* banana during growth

Age in days	Starch		Nitrogen		Starch : Nitrogen ratio in fruit
	Pulp	Peel	Pulp	Peel	
	gm.	gm.	gm.	gm.	
0	0.057	0.076	0.013	0.028	3.24
15	0.823	0.412	0.020	0.026	26.84
30	2.204	0.833	0.034	0.024	52.36
45	3.402	0.555	0.053	0.032	46.56
60	6.149	0.753	0.081	0.031	62.18
90	8.935	0.715	0.084	0.032	83.18
120	7.870	0.725	0.071	0.030	85.11

The rates of increase of starch and nitrogen in the pulp per fruit per day are shown in Fig. 8. Though the rate of starch

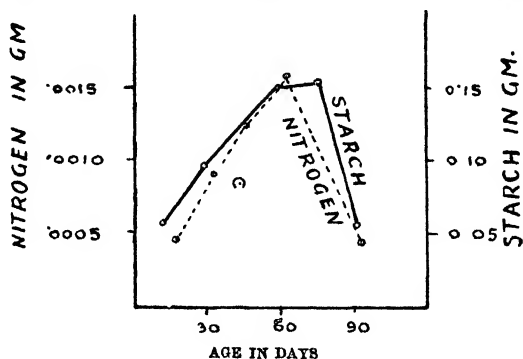


FIG. 8. Starch and Nitrogen Assimilation Per Fruit per Day

accumulation is about hundred times that of nitrogen, the trend of the two curves shows close similarity. The peak values in both cases are reached simultaneously at 60 days growth. The rate of nitrogen accumulation then suddenly declines while starch continues to accumulate at the same rate for another fortnight and then declines.

In Table 6 are also given the starch : nitrogen ratios of the fruit at the different stages of growth. The ratio increases continuously up to the 75th day and then remains steady as the starch accumulation has ceased. Singh (*loc. cit.*) reports a similar finding with regard to the mango and the guava.

The astringency of the pulp (Table 4) increases at first but disappears almost completely at maturity. In the peel (Table 5), however, the astringency increases continuously and is never removed.

The acid hydrolysable matter and the residue of the pulp (Table 4) representing respectively the cell-wall incrustations and cell-wall itself show an initial fall during the first 30 days and then remain steady. This shows that the accumulation of these constituents does not keep pace with that of starch during the first month of the growth of the fruit. After this they are synthesised at a more rapid rate and hence the percentages of these constituents remain steady.

The sugar contents of both peel and pulp are almost insignificant up to the stage of maturity. Rapid accumulation of sugars occurs, however, during the process of ripening. During the final stages of ripening only the reducing sugars predominate.

The chemical changes, like the physical ones, also point to a division of the life of the banana fruit up to maturity into

three distinct stages. The first one of 30 days is characterised by a rapid accumulation of starch and nitrogen. The next stage of another 30 days is marked by an increase in the synthesis of cell-wall and its incrustations. The remaining 60 days constitute the third or final phase after which the fruit begins to ripen. During this period the rate of accumulation of almost all constituents falls rapidly.

The analyses of the ash constituents of the banana are given in Table 7. The peel contains a higher percentage of ash than pulp. In the pulp, the ash percentage remains steady throughout whereas in the peel it increases with growth. Thus the rate of accumulation of ash constituents is greater in the peel than in the pulp. While the percentages of silica, lime and magnesia all decrease with growth, the percentage of potash and phosphoric acid in the pulp is steady throughout. Potash constitutes the most important mineral in the ash of both pulp and peel, amounting to more than 60 per cent. of the total ash.

TABLE 7

Mineral constituents of the *Basrai* banana at the different stages of growth
(Expressed as percentage of the fresh weight of pulp and peel on the day of sampling)

Age in days	Total Ash		SiO ₂		CaO		MgO		K ₂ O		P ₂ O ₅		Copper*		Iron*	
	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel
15	0.86	1.08	...	0.23	0.04	0.06	0.09	0.06	0.60	0.74	0.02	0.04	0.50	0.22	...	1.42
30	0.93	1.23	0.14	0.10	0.02	0.05	0.07	0.04	0.60	0.77	0.02	0.01	0.61	0.41	2.13	2.45
45	0.94	1.36	0.05	0.09	0.03	0.10	0.07	0.05	0.56	0.77	0.03	0.03	0.35	0.26	9.47	2.50
75	0.92	1.42	0.04	0.08	0.01	0.05	0.07	0.04	0.59	0.88	0.04	0.04	0.36	0.40	7.40	1.80
120	0.97	1.50	0.02	0.13	0.01	0.04	0.06	0.03	0.60	0.96	0.02	0.03	0.25	0.37	5.67	1.25

* Expressed as mgs. per 100 gms. of fresh weight.

TABLE 8

Potash content of the pulp per fruit of *Basrai* banana
and the rate of its assimilation during growth

Age in days	15	30	45	75	120
Potash (K ₂ O) in gm. ...	0.08	0.10	0.13	0.22	0.28
Rate of potash assimilation in gm. per day ...	—	0.0016	0.0018	0.0031	0.0030

In Table 8 are given the potash content of the pulp per fruit and the rate of accumulation of potash per fruit per day. The close similarity between rates of starch and potash accumulation is significant. Sorauer quoted by Brown (Ann. Bot., 1927, 41, 127) states that in carbohydrate storing plants, the amount of carbohydrate formed is directly dependent on the supply of potassium. Hence the importance of potassium in banana where the main activity is the synthesis of starch. In the apple, however, though it is rich in potassium, Brown (*loc. cit.*) did not find any direct correlation.

The percentage amount of copper in peel is more than that in the pulp in the later stages of growth. Bailey (Jour. Amer. Chem. Soc., 1912, 34, 1706) has recorded that the banana peel has a strong bactericidal action and has attributed it to the presence of copper.

TABLE 9

Nitrogen : phosphorus ratio in the pulp of the *Basari* banana at different stages of growth

Age in days	15	30	45	75	120
Nitrogen : Phosphorus ratio ...	7.80	10.80	9.00	—	9.70

The nitrogen : phosphorous ratio in plants has a special significance. A linear relation has been found to exist when both nitrogen and phosphorous are present in the same organic molecule. In the case of the banana pulp the ratio is almost constant at about 9.3 (Table 9). It appears, therefore, that most of the phosphorus is in the organic form, which perhaps accounts for the local popular belief that the banana is rich in phosphorous and is a brain food. In apples, no such linear relation was observed by Brown (*loc. cit.*), who concludes that 80 per cent. of the phosphorous of the apple is in the inorganic form.

CHANGES DURING RIPENING

For these studies the *Rajapuri* variety of banana was employed. In addition to the determination of the changes taking place in some of the important constituents, the respiratory and catalase activities of the fruit were also measured.

Chemical changes.—In the comparatively short period of ripening—about 10 to 12 days—very rapid changes occur in

the constituents of the banana. To investigate these changes, samples at short intervals were analysed. A number of fully matured bunches of the *Rajapuri* banana were harvested and placed in a well-ventilated room. At short intervals, one or two hands were removed and analysed. The results of analyses are given in Table 10. To avoid the variation caused by the fluctuations in the moisture content of pulp and peel, all the results are referred to the fresh weight of the pulp and peel on the day of harvesting, assuming that the total dry matter of the fruit remains constant during ripening.

During ripening the fruit loses considerable amount of moisture. This loss of moisture is not the same in pulp and peel. After the seventh day the pulp moisture increases, while in peel it continues to decrease rapidly. There is thus a transfer of water from peel to pulp. Gore (*loc. cit.*) has observed a similar phenomenon in bananas. Stratten (*loc. cit.*) attributes it to the sudden rise in osmotic pressure of the pulp sap, due to the formation of sugar.

The main feature of ripening is the formation of sugars from the hydrolysis of starch. Within the first four days the total sugar of pulp increases to about 12 per cent. This is accounted for by a similar fall in the concentration of alcohol-insoluble matter which consists mainly of starch. The sugar content of pulp reaches a maximum on about the eleventh day after which it begins to decrease. Gore (*loc. cit.*) observed a similar trend of changes in the varieties of banana he investigated. The changes in the sugar content of peel, though

TABLE 10

Changes in the different constituents of the *Rajapuri* banana during ripening

(Expressed as percentage of original fresh weight of pulp and peels)

Days after harvesting	Moisture		Total sugars		Reducing sugars		Non-reducing sugars		Alcohol-insoluble matter		Acidity	
	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel	Pulp	Peel
0	71.74	90.65	0.32	0.20	0.28	0.07	0.4	0.13	26.47	8.56	0.044	0.026
4	68.55	88.89	12.03	1.93	11.54	1.26	0.49	0.67	13.82	5.46	0.388	0.035
7	68.50	87.40	18.10	2.49	17.70	2.30	0.40	0.19	6.67	4.73	0.411	0.092
11	70.77	75.58	21.13	2.39	21.03	2.45	0.10	Nil	...	4.80	0.442	0.076
16	71.22	57.71	19.90	2.07	19.46	1.88	0.44	0.19	3.44	5.86	0.367	0.005

not so great as in the pulp, show a similar drift, with this difference, however, that the maximum concentration is reached a few days earlier. Almost all the sugar in this variety of banana is present in the form of reducing sugars. In some other varieties of banana (Table 1) non-reducing sugars occur in appreciable amounts. Salvador (Phillipine Jour. Sci., 1922, 20, 363) has published analyses of a number of varieties of Phillipine banana, which show a wide variation in their reducing and non-reducing sugar contents.

The acidities of both pulp and peel increase during ripening, reach a maximum at about the same time as the sugars and then decrease. Gane (New Phytologist, 1936, 35, 212) found the pH of the banana to decrease during ripening and then increase when the fruits become over-ripe.

Respiratory activity.—Banana bunches of three different degrees of maturity—immature, semi-mature and mature—were harvested and their rates of respiration recorded from day to day till they showed signs of decay. The results are given in Table 11 and Fig. 9. The rates of respiration of the samples on the

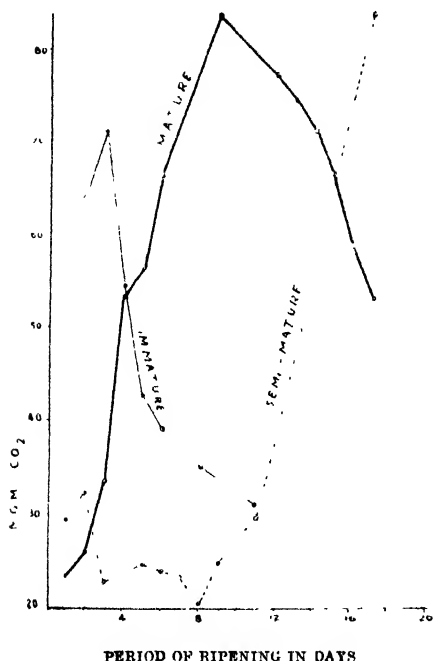


FIG. 9. Rate of Respiration of Fruit

first day after harvesting show that the respiratory activity decreases with advance of maturity. Immediately after harvesting, all the samples show an increase in the rate of respiration. It seems the plucking of the fruits from the stem has given a stimulus to the respiratory activity. Kidd (Nature, 1935, 135, 327) did not observe in apples any such stimulation due to plucking. Apples picked immature showed a downward trend from the very start.

In the immature fruits, after the initial rise in respiratory activity due to the plucking

stimulus, the rate of respiration continuously declined. Gradually the fruits became desiccated and brown in colour.

TABLE 11

Respiratory activity of the *Rajapuri* banana gathered at different stages of growth

(Expressed as mg. of CO_2 per Kg. per hour)

Days after harvesting	Rate of Respiration		
	Immature	Semi-mature	Mature
1	61.4	29.4	23.2
2	64.8	32.4	25.9
3	71.2	22.8	33.6
4	54.5	...	53.3
5	42.8	24.6	50.4
6	39.1	23.9	66.3
7	...	23.2	...
8	35.3	20.2	...
9	...	24.7	83.7
10
11	30.9	29.8	...
12	Rotting	...	77.3
13	"	...	74.5
14	"	...	71.4
15	"	...	66.6
16	"	...	58.9
17	"	83.7	53.2

In the semi-mature fruits, after the preliminary rise due to the plucking stimulus, the respiratory activity falls below the original value, then continues steady for sometime after which it suddenly rises to a high value in the next nine days. This rise is characteristic of the climacteric in fruits. As the fruits are only semi-mature, the onset of the climacteric is delayed for a few days.

In the mature fruits, the rate of respiration rises from the very beginning showing thereby that the onset of the climacteric is almost immediate. The maximum value here also is reached in about nine days and is about three times the respiratory activity at the start of the climacteric rise. Thereafter, the rate of respiration declines gradually but continuously without a break. A similar type of curve has been observed by Gore (*loc. cit.*), Onley (Bot. Gaz., 1926, 82, 415) and Hartshorn (Plant Physiol., 1931, 6, 467) for the respiration of the mature banana. But according to Gane (*loc. cit.*) the fall in rate of respiration, after the climacteric peak, is not continuous.

Catalase activity.—The catalase contents of both pulp and peel were separately estimated in the same samples used for determining the rate of respiration. In addition to the three, an over-mature sample has also been included for this study. The results are plotted in Figs. 10 to 13.

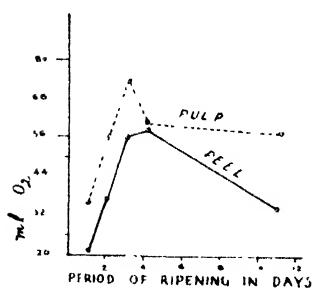


FIG. 10

Catalase Activity of Immature Fruits

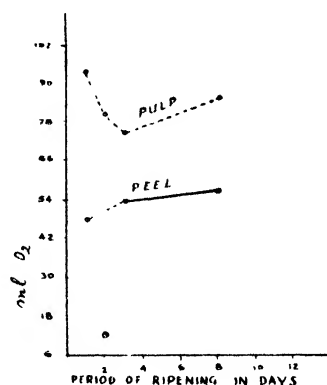


FIG. 11

Catalase Activity of Semi-mature Fruits

The catalase contents of both pulp and peel increase with growth and the pulp is more active than the peel. In the developing pears, Overholer (quoted by Harding, Iowa Agri. Expt. Sta. Res. Bull., 1935, 182, 317) found that the catalase decreased with growth.

After harvesting, the catalase contents of both pulp and peel of the first two samples—immature and semi-mature—fluctuate for a few days and then remain steady. The pulp is still more active than the peel. Both the samples, however, got desiccated and blackened without properly ripening.

In the mature and over-mature samples, however, the catalase activities of pulp and peel (Figs. 12 and 13) show very

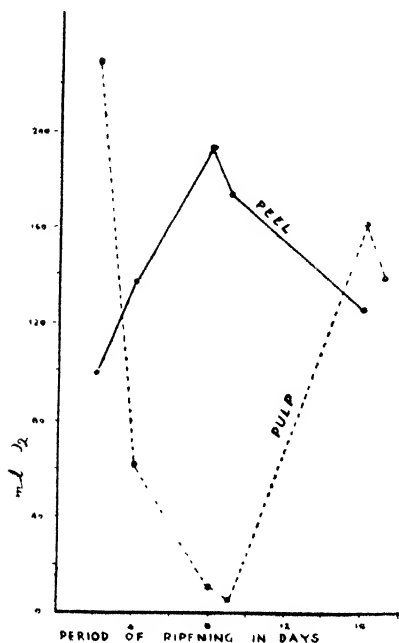


FIG. 12

Catalase Activity of Mature
Fruits

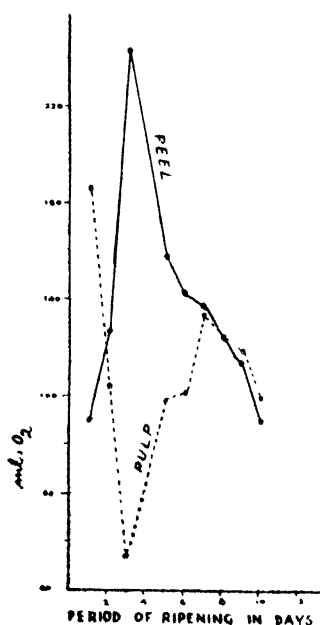


FIG. 13

Catalase Activity of Over-mature
Fruits

characteristic trend of changes during ripening. The catalase activity in peel increases while that in pulp decreases. The two curves for pulp and peel intersect in the mature sample two days after harvesting, and in the over-mature sample only one day after harvesting. The catalase activity of the peel attains the maximum at about the same time as the catalase activity of the pulp reaches the minimum. Then the two activities proceed at the same rate in opposite directions and their curves again meet after a few days after which the catalase activities in both pulp and peel simultaneously decline. The symmetrical natures of the curves for pulp and peel in both the samples is to be noted.

When the graphs of the third and fourth samples are compared, the importance of the picking maturity in the case of fruits becomes manifest. The interval between the date of harvesting and the second intersecting points of the catalase activities of pulp and peel during ripening may be taken to

represent the senescent phase of the life of the banana. In the third sample the span of senescent life extends over nearly a fortnight, while in the fourth sample it is only about six days. The fourth sample, when harvested, was more advanced in maturity which reduced its senescent period. Onley (*loc. cit.*) has observed a similar effect of picking maturity on the span of senescent life of the banana fruit.

While the catalase activities of both pulp and peel increase during growth, the respiratory activity decreases. As soon as maturity is reached and ripening starts, the catalase activity of the pulp begins to decrease while the catalase activity of the peel and the respiratory activities of the fruit both increase and attain their maximum values. At about the same time, the pulp catalase activity reaches its minimum value (Fig. 12). Neither of the two intersection points nor the maximum and minimum points on the catalase curves are, however, indicated on the respiratory curves.

The maximum concentration of sugars in the pulp occurs just after the hump in the respiratory curve is passed. This is about the same time or slightly earlier than the second intersection point of the catalase curves. At this point also the fruit possesses the best eating quality. Gane (*loc. cit.*) reports a similar finding in the varieties of banana he investigated. In apples, also according to Kidd and West (*Nature*, 1929, 123, 315), the best eating quality is attained after the respiratory hump is passed, while in pears it coincides with the respiratory hump.

SUMMARY

The physical and chemical changes occurring during the growth and ripening of the banana fruit have been studied. The catalase and respiratory activities of the fruit have also been investigated. The pulp and peel have been analysed separately.

The banana fruit takes about 120 days to mature on the plant. The process of ripening, however, is very rapid. It takes about eight to ten days after the mature fruits are removed from the plant.

The changes indicate three broad stages during the growing period of the fruit. The first stage of thirty days is characterised by a decreasing rate of growth. During the second stage, which also lasts for about thirty days, there is a sudden increase in the rate of growth which reaches a maximum. The

last sixty days constitute the third stage when the growth rate gradually declines and ultimately falls to zero.

The main activity of the fruit during growth is concentrated round the sythesis and storage of starch. Almost the whole of the starch is, however, hydrolysed into sugars during the process of ripening.

Potash constitutes a major portion of the ash content of the fruit. The nitrogen: phosphorus ratio is almost constant throughout the period of growth indicating that most of the phosphorus is present in an organic form.

The respiratory activity of the mature fruit is stimulated on harvesting and reaches the climacteric peak in about eight to ten days. The catalase activity of the pulp is greater than that of peel during the process of growth. During ripening, however, the catalase activity of the pulp at first declines to a maximum and then rises. The exact opposite takes place in the case of the peel.

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STALACTITES IN INDIA

By

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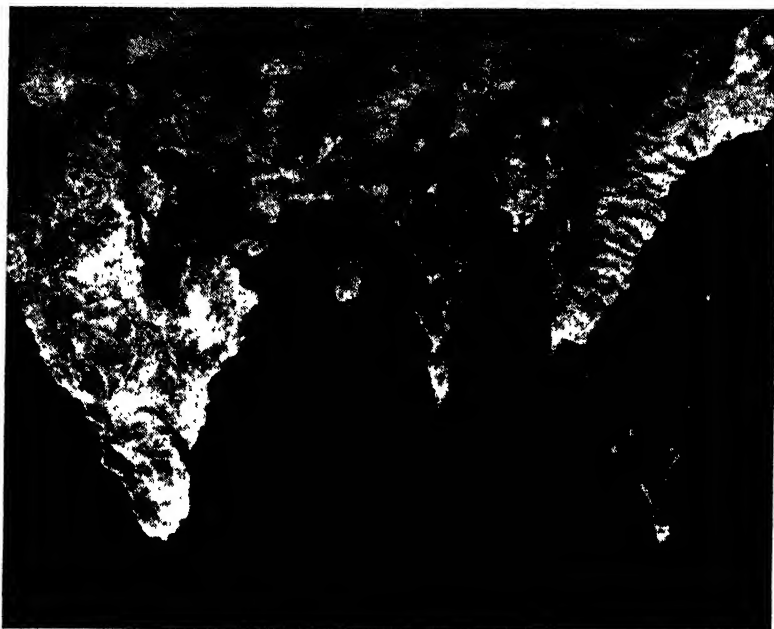
IT is only in English books that we read of Stalactite formations, giving references to places in the West only, *e.g.*, Ingleborough Cavern, Yorkshire; the caves at Cheddar and the Peak Cavern, Derbyshire; the Caverns at Jenolan, New South Wales. (Mellor's Modern Inorganic Chemistry, 1939, p. 279; The New Standard Encyclopaedia, The Times of India Publication, 1936, p. 1163).

On its passage through limestone rocks, percolating rain water gets saturated with soluble calcium bicarbonate. When it opens out through the roof of a cavern, it does so drippingly and gets exposed to the atmosphere. With the escape of some carbon dioxide from the solution, the insoluble calcium carbonate falls out, each drop contributing its own little share. In doing so the calcium carbonate assumes the forms of small cylindrical, porous, if not hollow, tubes, or of the teats of a cow or of a sheep, later on developing into forms resembling the trunks of elephants, tapering downwards, even with wrinkles and pimples all over the surface, with a round hollow opening at the base. The trunks swell into wide pillars and fill up cavities.

We find at Rāmling Cavern (14 miles from Kolhapur) old temples being completely blocked by or embedded under such rocks. It will be interesting to measure the rate at which these calcareous deposits grow, which are known to do at an astounding rate of even twelve inches per month, as in the case of San Filippo springs, Tuscany, Italy. (*Ibid.* p. 279). And yet, this rate is nothing as compared to the rate that “क्षणावधि शैलौदक” (Kṣhaṇavedhi Shailodaka), referred to below, will show. We have not met with such a sample of water.

The above description of the Stalactite rock formation is given from what we actually observe at Rāmling (*Vide* photo-

graph). The photograph is of the ceiling of the temple-room,



STALACTITES AT RĀMLING

which is only about ten feet in length, about six feet in width and about eight feet in height. To avoid the blocking of this room (as is the fate of some other adjoining temples), due to the downward growth of the ceiling rock, it is chiselled out once in three or four years by the worshiper of the God Rāmling. The minimum diameter of the tubular forms is $\frac{1}{4}$ inch; maximum about one foot. The broad bases at the top grow wider and even meet into one. Such a rock portion develops new smaller tubules.

The authors have visited a few such other places. These are invariably where temples of Hindu Gods, especially Shiva and Goddess Pārvati, have been installed, and visited in thousands by devotees during annual fairs and festivities. In fact, it can well be observed that, such places of natural interest, after being discovered by the ancient Seers, or should we say, men of science, were particularly protected or prevented from getting into oblivion, by turning them into temples or sacred places for the common people to visit. We mention a few places which either or both of us have visited. There are many more of which we are told; and yet a greater number that are mentioned in ancient

Sanskrit literature. There are the "Shukāchārya Hills" about 22 miles from Karad, off the roadway to Pandharpur and Vite. From this place we have specimens of pieces of wood, embedded in the Stalactite rocks. There is another place by name "Siddheshwar," situated near the village Kalawai, about 20 miles from Nasik, where such waters are found. "Baneshwar" is still another place, for such waters in Maharashtra, off the motor road, to the right, as we drive from Poona to Bhor, past the tunnel. Hrisheekesha in the Punjab is noted to be in possession of such a "Zarna" (spring) giving rise to Stalactite formations.

These waters and these rocks (Stalactites) were known to Ancient India, in so many terms, being used for very definite purposes, even by reducing the rocks to the metal, or what they called "सत्त्वम्" (Satvam), by the special metallurgical methods. The following extracts testify to this view:—

नागनासिकाभिधानं चन्द्रोदकममृतमाप्तकाठिन्यम् ।
 रसवैक्रान्तकमेवम् (बध्नाति रसं स्वसत्त्वेन) ॥ १ ॥
 नानाविधसंस्थानं निर्जरशिखरिशिखरसम्भूतम् ।
 धारोदम्भसि श्रेष्ठं तदश्म शैलोदकं प्राप्य ॥ २ ॥
 भस्माद्वयेन हठतो ध्मातव्यं पञ्चमाहिषसुबद्धम् ।
 दत्त्वा दशांशस्वर्जिकपट्टकणगुजिकाक्षरान् ॥ ३ ॥
 तद्रूच्छति कठिनत्वं मुञ्चति सत्त्वं स्फुल्लिङ्गकाकारम् ।
 मुक्तानिकरप्रायं ग्राह्यं तत्काचमधिवर्ज्यं ॥ ४ ॥

(10th Avabodha, "Rasahridaya" by Sreemadgovindabhagavatpādāh, 800 A. D., edited by Kale and Acharya, Nirnaya Sagar Press, 1911).

[Translation : The Rasavaikrānta, by name "Nāganāsika,"—resembling the trunk of an elephant—which is nothing but the once nectar-like water, cool like the lunar rays, now turned into a hard rock, is potent enough to transform, by its own metal or "Satvam", mercury into a form stable to heat. This is obtainable at various places on the peaks of mountains, the abodes of Gods. Taking the Shailodaka, the water, or the best of all, the stone formed of the dripping waters, it should be thoroughly admixed with the five products of the she-buffalo (*viz.*, milk, curds, ghee, urine and dung) and with the fluxes, sodium carbonate, rock-salt, borax and the salts of the "Gunja" herb, each one taken one tenth in weight of the original stalactite-stone, and made into balls and fired, blowing strongly with a pair of hand-bellows. This turns into a hard mass, which is

broken up, and the slag discarded, yields an active principle (Satvam) blazing like fire and appearing like a lustrous heap of pearls].¹

Thus what was known as "Rasavaikrānta" was or is the Stalactite. There are also enumerated the places where the Shailodakas, from which the Rasavaikrāntas are formed, were found, one of which was:—

सह्याचले पुरे देव्याः क्षीरक्षेत्रस्य सन्निधौ ।

शैलोदकं कोटिवेधि.....॥

(12th Patala, "Rasāriṇava," before 100 A. D., edited by the Royal Asiatic Society, Calcutta).

[Translation: There is, in the Sahya Mountains, near the place "Ksheera-Kshetra" and in front of the temple of the Goddess, the Shailodaka, acting miraculously].

First, of all the spring waters, *e.g.*, Ushnodaka (hot springs), Raktodaka (red waters), Vishodaka (poisonous waters), Amritodaka (nectar-like waters), Chandrodaka (lunar waters) [Bhāratēya Rasāyan Shāstra by T. G. Kale, 1912, p. 92], Shailodaka was to be discovered as follows, as also its degree of saturation :

तज्जलं शुभयोगे तुम्बिपात्रेण गृहीत्वा घटान्तर्गत मध्ये धृत्वा क्षणवेधि, दिनवेधि, त्रिदिनवेधि वा पक्षवेधि वा मासवेधि वा द्विमासवेधि वा त्रिमासवेधि वा षण्मासवेधि वा वर्षवेधि वा त्रिवर्षवेधि एवं जलं स्थाने स्थाने भवति तद् ग्राह्यम् । तस्य परीक्षायाः क्रियाः—

द्विगुलं हरितालं च गन्धकं च मनः शिला ।

एषां गन्धापहारं यत्कुरुते तच्च वेधकम् ॥

गन्धकं तालकं चैव तोयपूर्णं घटे क्षिपेत् ।

यदा तद्बुद्बुदाकारं तदा शैलोदकं भवेत् ॥

(Bhuti-prakarāṇa, "Shaktyāvatāra," old manuscript, date not determined).

[Translation: On an auspicious day, the water is to be drawn by the pail of the bottle-gourd (preferably a bitter

1. The method remains to be copied in the laboratory. It is not unlikely that we may not succeed in the attempt. Still it is a prescribed method by which they did it then. It may be that we fail to get the exact proportions of all the exact chemicals or substances, *e.g.*, "गुञ्जिकाक्षारान्" may mean the salts of either the berries or the whole plant of the "Gunja" herb, perhaps of a particular species; or the Gunjikas and some other salts, commonly known and always used in one lot and in equal proportions.

variety) and stored in an earthen vessel. The waters collected from the various places are of different potencies, measured by the time required for the falling out of the solute from the solutions, *viz.*, just a moment, one day, three days, a fortnight, a month, two months, three months, six months, one year or three years. The particular spring water is Shailodaka if it gives effervescence with sulphur or an orpiment; if in addition, cinnabar, yellow and red orpiments and sulphur are turned odourless, on being treated with the water, the latter is "Vedhaka" (impregnating)].

They knew that a variety of water known as "Weshtaka" (enveloping) would envelop any solid immersed in it and thus protect it from any further putrefaction. Nay, we have reasons to believe that they used to preserve, in particular, fruits, seeds and herbs of medicinal value, in such waters, which would envelop them with layers of calcareous deposits. These enveloping stones would be broken open when the enveloped materials would be required for future use. In fact there is a special chapter by name "Shailodaka-kalpa" in the twelfth Patala of the big Work "Shaktyāvatāra," already referred to, in which are found the following lines:—

अन्वेषयेत्प्रयत्नेन शैलोदककृतं रसम् ।

[One should seek to obtain mercury treated with "Shailodaka"].

.....
शैलोदकमिदं तोयं बहुतत्त्वगुणान्वितम् ।

[This water, the "Shailodaka" possesses very valuable properties].

.....
आदौ शैलोदकं दिव्यं सर्वेषामेव..... ।

[The supernatural and wonderful "Shailodaka" tops the list of the different mineral waters].

.....
औषधमनुपानं च मित्रं चैव पृथग्जलैः ।

[For the various medicines the different waters are administered as vehicles (Anupāna)].

Thus does this Work deal with the different Shailodakas, their further formations, and the applications of either. This

subject is treated also in the twelfth Patala of the "Rasārṇava", in which the 291st stanza further specifically says:

सर्वं समफलं भवेत् ।

[The Shailodakas of all the different potencies ultimately give identical results].

Furthermore, the Stalagmite formations had not escaped the notice of the ancient scientists, it is interesting to discover from the same works. These were recommended for identical applications. Thus—

कर्दमापो महीशैलं शिलां चेति चतुर्विधम् ।

[There are the four types: the mud, the water, the Stalagmite and the Stalactite].

शैलोदके विनिक्षिप्य भूशैले कर्दमेऽपि वा ।

[By placing either in Shailodaka, Stalagmite (after pounding it into paste) or even in its mud].

They had realized that for whatever purpose one could be used, the others could be replaced with equal effect, or that all of them contained the same chemical substance, whether it be the water itself (Shailodaka), the loose mud from the same (Kardama), or either of the two formations, *viz.*, the Stalactite (Shilā) or the Stalagmite (Mahec-shaila or Bhu-shaila or Bhumi-shaila, as differently named elsewhere), meaning the rock formed from the floor upwards.

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A DERIVATION OF THE SCHRÖDINGER WAVE EQUATION

By

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INTRODUCTION

THE famous Schrödinger wave equation has been derived in several ways. But none of them is both simple and rigorous. The derivation given below is one such. Besides, the very mode of derivation brings out certain important peculiarities of wave mechanics.

With the advent of the theory of relativity, modern mathematical physics never makes use of any assumption which cannot be experimentally verified but permits well-established experimental results to be used. This principle is adhered to in the following derivation.

The Derivation

Suppose we have a distribution of property,

$$y=f(x)$$

Consider the equation

$$y=f(x-vt)$$

If we change the origin from O to O₁ such that

$$OO_1=vt$$

the new function will be

$$y_1=f(x_1)$$

Therefore, $y=f(x-vt)$ represents the progression of a property $y=f(x)$ with a velocity, v , and, while this progresses, there is no change of form. This is the most general mathematical definition of wave motion.

Consider the form of the differential equation for such a wave motion.

$$\frac{\delta^2 y}{\delta x^2} = f''(x - vt)$$

$$\frac{\delta^2 y}{\delta t^2} = v^2 f''(x - vt)$$

$$\therefore v^2 \frac{\delta^2 y}{\delta x^2} = \frac{\delta^2 y}{\delta t^2}$$

We shall here replace y by ψ as that would be convenient when we go to consider the three dimensional case. We then get

$$v^2 \frac{\delta^2 \psi}{\delta x^2} = \frac{\delta^2 \psi}{\delta t^2} \quad \dots \quad \dots \quad (1)$$

Equation (1) is the general differential equation of wave motion. General solutions of this equation can be obtained satisfying certain boundary conditions. We know from the theory of differential equations that a solution of the equation can be represented as the sum of other solutions. By Fourier's theorem, any function can be analysed into a number of simple harmonic components. Therefore, we can take, for the solution of the wave equation, a simple harmonic form as a representative solution. (It is this assumption that leads to an apparent contradiction to be referred to later). When we do so, we get,

$$\psi = A \cos 2\pi\nu \left(t - \frac{x}{v} \right) \quad \dots \quad (2)$$

" ν " is called the frequency of the wave. " λ " is called the wave-length of the wave and measures the distance between two successive points on the wave which are in the same phase, i.e., between two successive points at which ψ has the same value. " ν " represents the number of wave lengths described by the progression of the wave in one second. It follows, therefore,

$$\nu\lambda = v \quad \dots \quad \dots \quad (3)$$

" ν ", therefore, defines the "phase velocity" of the wave.

From (2), we have

$$\frac{\delta^2 \psi}{\delta t^2} = -4\pi^2\nu^2\psi \quad \dots \quad \dots \quad (4)$$

Substituting from (4) in (1), we get

$$v^2 \frac{\partial^2 \psi}{\partial x^2} = -4\pi^2 v^2 \psi \quad \dots \quad \dots \quad (5)$$

$$\therefore \frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 v^2}{v^2} \psi = 0$$

$$\therefore \frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 \psi}{\lambda^2} = 0 \quad \dots \quad \dots \quad (6)$$

From the experiments of Davisson and Germer, G. P. Thomson, Stern and others, we know that particles of mass, m , and velocity, w , behave in their propagation through space like waves with wave-length given by

$$\lambda = \frac{h}{m w} \quad \dots \quad \dots \quad \dots \quad (7)$$

where h = planck's constant.

Substituting from (7) in (6), we get,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 m^2}{h^2} w^2 \psi = 0 \quad \dots \quad \dots \quad (8)$$

If E is the total energy of the particle, and V its kinetic energy, we have

$$\begin{aligned} \frac{1}{2} m w^2 &= E - V \\ \therefore w^2 &= \frac{2(E - V)}{m} \quad \dots \quad \dots \quad \dots \quad (9) \end{aligned}$$

Substituting from (9) in (8), we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots \quad \dots \quad (10)$$

This is the one dimensional Schrödinger wave equation. If we apply the same arguments to the three dimensional case, we get

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots \quad \dots \quad (11)$$

Let us now consider the implications of the derivation.

By (3) and (7), we have

$$\begin{aligned} \lambda &= \frac{v}{\nu} = \frac{h}{m w} \\ \therefore h \nu &= m w v \quad \dots \quad \dots \quad \dots \quad (12) \end{aligned}$$

$$\therefore v = \frac{h \nu}{m w} \quad \dots \quad \dots \quad \dots \quad (13)$$

By the quantum theory, we know that

$h\nu$ = energy of the quantum and by the theory of relativity,

energy of the quantum = mc^2 where m is the mass associated with the quantum. Hence

$$h\nu = mc^2$$

$$\therefore \frac{h\nu}{m} = c^2 \quad \dots \quad \dots \quad \dots \quad \dots \quad (14)$$

$$\therefore v = \frac{c^2}{w} \quad \dots \quad \dots \quad \dots \quad \dots \quad (15)$$

Equation (15) leads to two interesting conclusions :—

(a) $v > c$, an apparent contradiction to the theory of relativity.

(b) $v \neq w$

Although the wave equation was derived in a different manner, these appeared as difficulties in the early stages of the development of wave mechanics. In the above derivation, these difficulties appear quite naturally. We know, however, that they are at present no longer difficulties.

“(b)” appears as a difficulty because we take a simple harmonic solution as a representative solution for the wave equation. The fact is that ψ has to be normalised so that $|\psi|^2$ gives the probability of finding the particle at the point under consideration. When this is done, it will be found that the particle has associated with it a wave group and the group velocity equals w ; “ v ” is only the phase velocity of the associated wave and can exceed “ c ” without violating the principles of relativity.

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ABSTRACTS OF Ph.D. THESES

I—STUDIES IN COUMARINS. BY MR. S. M. SETHNA, M.Sc.,
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Part I: Section (i). Pechmann Condensation of methyl B-resorcyrate with ethyl Acetoacetate and ethyl α -alkyl Acetoacetates:—Methyl B-resorcyrate has been condensed with ethylacetoacetate and ethyl α -alkyl acetoacetates (*c.g.*, ethyl α -methyl, α -ethyl, α -propyl, and α -butyl acetoacetates) in presence of conc. or 80% H_2SO_4 and the products whose constitutions have been proved have been found to be 7 hydroxy coumarin derivatives.

The condensation of even ethyl- α -butyl acetoacetate with methyl B-resorcyrate shows that the presence of carbmethoxy group retards the Pechmann reaction less than the nitro group, as 4-nitro resorcinol condenses only with ethyl acetoacetate and not with ethyl α -alkyl acetoacetates (Chakravarti and Banerjee, J. Ind. Chem. Soc., 1937, 14, 37).

Section (ii). Pechmann condensation of methyl B-resorcyrate with other B-ketonic esters:—Methyl B-resorcyrate has been condensed with ethyl α -benzyl, α -benzoyl and α -chloro acetoacetates and also with ethyl acetone dicarboxylate. The products obtained, whose constitutions have been proved, have been found to be 7-hydroxy coumarin derivatives.

Part II: Aluminium Chloride, a new Reagent for the Condensation of B-ketonic esters with Phenols. Section (i). Condensation of methyl B-resorcyrate with ethylacetoacetate:—It has been found that when methyl B-resorcyrate is condensed with ethylacetoacetate in presence of anhydrous aluminium chloride, a new reagent for the condensation of B-ketonic esters with phenols, instead of sulphuric acid, the condensation proceeds differently with the formation of methyl 5-hydroxy-4-methyl coumarin-6-carboxylate in good yield which on hydrolysis and subsequent decarboxylation gave 5-hydroxy-4-methyl coumarin. The unique action of aluminium chloride in affording a 5-hydroxy coumarin derivative in this condensation is noteworthy as it

makes easily accessible the 5-hydroxy coumarin derivatives which are substances of synthetical importance and which till now were accessible with great difficulty.

The mechanism of the formation of 5-hydroxy coumarin derivatives when aluminium chloride is used as a condensing agent has been discussed.

Section (ii). Condensation of methyl-2:4-dihydroxy-5-ethyl benzoate with ethylacetoacetate:—Methyl 2-4-dihydroxy 5-ethyl benzoate condenses with ethylacetoacetate in presence of Aluminium Chloride to give methyl 5-hydroxy-4-methyl 8-ethyl coumarin 6-carboxylate which on hydrolysis and subsequent decarboxylation gave 5-hydroxy 4-methyl 8-ethyl coumarin. Conc. H_2SO_4 when used as a condensing agent in place of aluminium chloride gave the same coumarin ester, but, in slightly inferior yield.

Section (iii). Condensation of Simple Polyhydric Phenols with ethylacetoacetate:—The condensation of ethyl acetoacetate with various polyhydric phenols has been studied using aluminium chloride dissolved in dry ether or in nitrobenzene as the condensing agent. In all cases studied, the products, obtained in good yield, are the same as obtained with H_2SO_4 as condensing agent.

Section (iv). Condensation of methyl phloroglucinate with ethylacetoacetate:—Methyl phloroglucinate has been condensed with ethylacetoacetate in presence of anhydrous aluminium chloride. The product obtained has been found to be methyl-5:7 dihydroxy-4-methyl coumarin-6 (or-8) carboxylate. This on simultaneous hydrolysis and decarboxylation gave the known 5:7-dihydroxy-4-methyl coumarin. Conc. H_2SO_4 as condensing agent in place of AlCl_3 also gave the same coumarin ester.

Part III: Pechmann Condensation of P-Orsellinic Acid with Ethyl Acetoacetate—Synthesis of 7-Hydroxy 4:5 Dimethyl Coumarin:—p-Orsellinic acid has been condensed with ethyl acetoacetate in the presence of sulphuric acid. The product obtained has been assigned the constitution of 7-hydroxy 4:5-dimethyl coumarin-8-carboxylic acid. This on decarboxylation gave a product which is different from the chromone-7-hydroxy-2:5-dimethyl chromone obtained from the B-diketone which was obtained by the Claisen condensation of the dimethyl ether of orcacetophenone with ethylacetate. The decarboxylated product has therefore been assigned the constitution of the hitherto unknown 7-hydroxy 4:5-dimethyl coumarin which cannot be

prepared by the condensation of orcinol with ethylacetoacetate, as this condensation yields 5-hydroxy 4:7-dimethyl coumarin (Collie and Chrystall, J., 1907, 1804).

Part IV: Section (i). Kostanecki-Robinson Reaction on Orcacetophenone and its Monomethyl ether with (1) Sodium Acetate and Acetic Anhydride, (2) Sodium Propionate and Propionic Anhydride, (3) Sodium Butyrate and Butyric Anhydride and (4) Sodium Benzoate and Benzoic Anhydride:—Orcacetophenone on acetylation with sodium acetate and Acetic anhydride gave a product to which the provisional constitution of 7-acetoxy-4-acetomethyl-5-methyl coumarin has been assigned. This on treatment with conc. H_2SO_4 gave 7-hydroxy-4-acetomethyl-5-methyl coumarin which on treatment with dilute sodium hydroxide was converted into 7-hydroxy 4-5-dimethyl coumarin; this structure being assigned because it is identical with the product obtained on decarboxylation of the coumaarin carboxylic acid obtained on condensation of *p*-orsellinic acid with ethyl acetoacetate described in the previous part.

Orcacetophenone monomethylether gave on a similar acetylation 7-methoxy-4-acetomethyl-5-methyl coumarin.

The exclusive formation of the coumarin on acetylation of orcacetophenone and its monomethyl ether is unexpected as resacetophenone and its monomethyl ether give exclusively a chromone in the above reaction (Kostanecki and Rozycki, Ber., 1901, 34, 102). The formation of C-acyl coumarins which has been observed for the first time in Kostanecki-Robinson reaction is of interest.

Propionylation and butyrylation of orcacetophenone gave the analogous 4-substituted coumarin derivatives.

A point of interest is the development of the method for the step-wise elimination of O-acyl and C-acyl groups, by the successive use of conc. H_2SO_4 and alkali. Conc. H_2SO_4 only removes the O-acyl group keeping the C-acyl group (in the pyrone ring) intact.

The mechanism of the formation of 4-acyl methyl coumarins is suggested. The '6' methyl group in orcacetophenone seems to have a profound influence on the course of the Kostanecki-Robinson reaction.

Benzoylation of orcacetophenone gave 7-benzoyloxy-3-benzoyl-5-methyl flavone which on treatment with conc.

H₂SO₄ gave 7-hydroxy-3-benzoyl-5-methyl flavone and on treatment with alcoholic KOH gave 7-hydroxy-5-methyl flavone.

Section (ii). Synthesis of 7-hydroxy-2-alkyl-5-methyl chromones.—The syntheses of 7-hydroxy-2-5-dimethyl chromone, 7-hydroxy-2-ethyl-5-methyl chromone and 7-hydroxy-2-propyl-5-methyl chromone has been carried out for proving the coumarin structure of the compounds obtained in Section (i) of this part. Chromones have been prepared by the Claisen condensation of orcacetophenone dimethyl ether with ethyl acetate, ethyl propionate and ethyl butyrate and subsequent ring closure of the β -diketones formed.

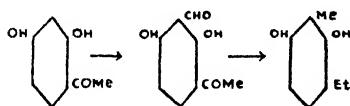
Part V: The Condensation of Orcacetophenone Monomethyl ether with Ethyl Acetate, Ethyl Propionate and Ethyl Butyrate.—Orcacetophenone monomethyl ether on Claisen Condensation with ethyl acetate gave instead of the expected β -diketone, presumably a cinnamic acid derivative which on heating with dilute HCl gave 7-methoxy-4:5-dimethyl coumarin. Orcacetophenone monomethyl ether on similar condensation with ethyl propionate and ethyl butyrate gave the corresponding substituted cinnamic acids which on heating with dil. HCl gave 7-methoxy 3:4:5-trimethyl coumarin and 7-methoxy 3-ethyl-4:5-dimethyl coumarin respectively. The formation of a cinnamic acid derivative in the Claisen condensation of O-hydroxy ketones with esters has not been observed before. The formation of cinnamic acid derivatives in place of the expected β -diketones is therefore of interest. The '6' methyl group in orcacetophenone seems to have a profound influence on the course of this condensation.

S. M. S.

II—"Y-SUBSTITUTION IN THE RESORCINOL NUCLEUS". BY
MR. H. A. SHAH, M.Sc., ROYAL INSTITUTE OF SCIENCE,
BOMBAY.

Part I: Gattermann reaction on phenolic ketones—Synthesis of hydroxy formyl phenyl ketones.—Application of Shah and Laiwalla's (J. 1938, 1828) modified Gattermann reaction to polyhydroxy phenolic ketones yields hydroxy-3-formyl phenylketones—a class of compounds hitherto unknown, the formyl group entering when possible the usually inaccessible Y-position in the resorcinol nucleus.

Resacetophenone on formylation gave 2-4-dihydroxy-3-formyl acetophenone (Shah and Shah, J. 1939, 132) whose constitution was established by its Clemmensen reduction to 4-ethyl-2-methyl resorcinol. (Robinson and Shah, J. 1934, 1494).

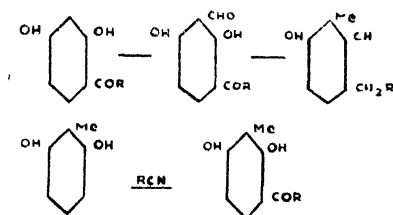


2-4-Dihydroxy-5-ethyl acetophenone on formylation afforded 2-4-dihydroxy-3-formyl-5-ethyl acetophenone. However, the Gattermann reaction on 2-4-dihydroxy-5-bromo acetophenone, 2-4-dihydroxy-5-nitro-acetophenone, paenol, iso-paenol and 2-4-dimethoxy resacetophenone did not succeed.

2-Acetyl resorcinol on formylation afforded 2-4-dihydroxy 3-acetyl benzaldehyde, which on Clemmensen reduction afforded—4-methyl-2-ethyl resorcinol (Robinson and Shah, loc. cit.).

Orsacetophenone and phloracetophenone similarly afforded 2-4-dihydroxy-3-formyl 6-methyl acetophenone and 2-4-6-trihydroxy-3-formyl acetophenone respectively. Gall acetophenone however did not undergo the condensation.

Gattermann reaction on various 4-acyl resorcinols, *viz.*, respropiofenone ($R = C_2H_5$), resbutyrophenone ($R = C_3H_7$) 2-4-dihydroxy benzophenone ($R = Ph$) and 2-4-dihydroxy-phenyl benzyl ketone ($R = CH_2Ph$) afforded, 2-4-dihydroxy-3-formyl propiofenone 2-4-dihydroxy-3-formyl butyrophenone, 2-4-dihydroxy-3-formyl benzophenone and 2-4-dihydroxy-3-formyl-phenyl-benzyl ketone respectively. Their constitutions were established by their Clemmensen reduction to 2-methyl-4-alkyl resorcinols which were identical with authentic specimen of the phenols prepared by the reduction of 3-methyl-4-acyl-resorcinols prepared by the application of the Hoesch reaction to 2-methyl resorcinol and the corresponding nitriles.



ω -Chlororesacetophenone on formylation afforded 2-4-dihydroxy-3-formyl ω -chloroacetophenone. ω -Methoxy resacetophenone however did not condense.

The ketone aldehydes have been condensed by the Knoevenagel method with ethyl acetoacetate, ethyl malonate and cyanoacetic acid to give interesting coumarin derivatives.

The orientation of the aldehydes from resacetophenone, orsacetophenone and other 4-acyl resorcinols in which the formyl group enters the 3-position instead of the usual 5-position is of interest. These results are best explained on the view that the chelation between hydroxyl and the acyl group stabilises the double bond in the resorcinol nucleus; the carbon atom in the 3-position which is united by a double bond to the carbon atom bearing the 4-hydroxyl group is the point of attack.

The syntheses of hydroxy formyl phenyl ketones opens up various possibilities for the synthesis of heterocyclic compounds containing oxygen in the ring like chromone- α -pyrones furo-coumarones, furo-chromones and furo-coumarins.

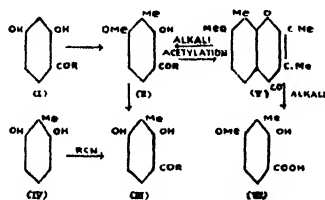
Part II: Synthesis of 2-6-dihydroxy-3-ethyl benzaldehyde:— Application of Shah and Laiwalla's modified Gattermann reaction to methyl 2-4-dihydroxy-5-ethyl benzoate afforded methyl 2-4-dihydroxy-3-formyl-5-ethyl benzoate which on hydrolysis and subsequent decarboxylation gave 2-6-dihydroxy-3-ethyl benzaldehyde a Y-resorcyaldehyde derivative.

The Gattermann reaction on methyl-2-4-dihydroxy-5-bromo resorcyate and methyl-2-4-dihydroxy-5-nitro resorcyate did not succeed.

*Part III: Nuclear methylation of 4-acyl resorcinols:—*In connection with our work on the syntheses of hydroxy-formyl-phenyl ketones, (Part I) it was necessary to synthesise 2-methyl-4-alkyl resorcinols, by an unambiguous method; hence the nuclear methylation of various 4-acyl resorcinols has been studied.

Respropiphenone (I) ($R = C_2H_5$) on nuclear methylation

afforded 2-hydroxy-4-methoxy-3-methyl-propiophenone, (II) demethylation of which gave 2-4-dihydroxy-3-methyl propiophenone which was identical with 2-4-dihydroxy-3-methyl propiophenone (III) prepared by the application of the Hoesch reaction to 2-



methyl resorcinol (IV) and propio-nitrile. Kostanecki acetylation of the ketone (II) with sodium acetate and acetic anhydride afforded 7-methoxy-2-3-8-trimethyl chromone (V) whose constitution was established by its alkaline hydrolysis to the ketone (II) and 2-hydroxy-4-methoxy-3-methyl benzoic acid (VI).

Similarly the nuclear methylation of resbutyrophenone, 2-4-dihydroxy-phenyl-benzyl ketone and 2-4-dihydroxy benzo-phenone has been studied. The mechanism of nuclear methylation has also been explained.

Part IV: Synthesis of 5-hydroxy coumarin:—4-methyl-5-hydroxy coumarin which was hitherto inaccessible is now readily available by the condensation of methyl- β -resorcy-late and resacetophenone with ethylacetoacetate in presence of aluminium chloride dissolved in nitrobenzene. Obviously 5-hydroxy coumarin cannot be synthesised by this method.

5-hydroxy coumarin has now been synthesised starting from methyl 2-4-dihydroxy 3-formyl benzoate (Shah and Laiwalla, J. 1938, 1828).

Methyl 2-4-dihydroxy-3-formyl benzoate on methylation afforded methyl-2-hydroxy-3-formyl 4-methoxy benzoate which on condensation with ethyl malonate afforded ethyl 5-methoxy-8-carbomethoxy-coumarin-3-carboxylate, hydrolysis of which afforded 5-methoxy-coumarin-3-8-dicarboxylic acid. The foregoing acid on decarboxylation gave 5-methoxy coumarin demethylation of which afforded 5-hydroxy coumarin.

Part V: Synthesis of furo-3'-methyl-5-6-(4'-5') coumarin and furo-3'-ethyl-5-6-(4'-5') coumarin:—Furo-coumarins derived from 5-hydroxy coumarin are not known except for the synthesis of 3-4'-dimethyl-5'-6'-furo coumarin (Kelkar and Limaye, Rasayanam, 1938, I, 151) from 5-hydroxy-6-acetyl-4-methyl coumarin (Sethna, Shah and Shah, J. 1938, 228).

Ethyl-5-hydroxy-6-acetyl coumarin-3-carboxylate on condensation with ethyl bromacetate afforded ethyl 3-carboxyl-6-acetyl coumarin-5-0-acetic ester hydrolysis of which 3-carboxyl-6-acetyl coumarin-5-0-acetic acid. The acid on treatment with boiling acetic anhydride containing sodium acetate afforded Furo-3'-methyl-5-6-(4'-5') coumarin-3-carboxylic acid decarboxylation of which afforded Furo-3'-methyl-5-6-(4'-5') coumarin.

Ethyl-5-hydroxy-6-propionyl coumarin 3-carboxylate similarly afforded Furo 3'-ethyl-5-6-(4'-5') coumarin.

H. A. S.

III—"STUDIES IN THE CHEMISTRY OF MILK". BY MR. B. N. ACHARYA, M.Sc., CHEMISTRY LABORATORY, WILSON COLLEGE, BOMBAY.

Part I: Compounds of Phosphorus in Milk:—Although phosphorus compounds in milk have been studied by many in

the field, their classification and general nature are still incomplete and obscure. An attempt to find the nature of different compounds of phosphorus in the buffalo's milk available in Bombay City, is made in this part. Some of phosphorus compounds in milk are soluble in acid but others are insoluble. In the acid soluble portion, the existence of five independent types of phosphorus—ortho, pyro, organic phosphorus compounds insoluble in barium hydroxide at pH 9 and hydrolysable as well as non-hydrolysable organic phosphorus compounds soluble at pH 9, has been established. The acid insoluble portion of phosphorus compounds was shown to consist of casein phosphorus and lipid phosphorus. The amount of phosphorus present in these seven varieties are estimated directly. It is mentioned that easily hydrolysable organic phosphorus and pyro phosphorus compounds are unstable and are changed over to the ortho variety on standing or heating.

Part II: Phosphorus, calcium and Magnesium in milk :— Calcium and magnesium are capable of forming with phosphorus, both soluble and insoluble salts; but the mode of formation of the latter is not yet properly known. In this investigation estimations of phosphorus, calcium and magnesium were made under varying conditions. From the results it is concluded that the portion of milk insoluble in acid is mostly casein which adsorbed some ions of calcium and magnesium. The portion soluble in acid but insoluble in water consists of tricalcium and magnesium phosphates and organic phosphorus compounds. The scum which is formed after heating the milk is derived both from the acid insoluble and acid soluble portions. On dialysis some acid-insoluble portion becomes water-soluble. It is suggested that the water soluble portion of milk consists of acid phosphates of calcium and magnesium.

*Part III: Milk powders :—*Milk in the form of dry powders is available in the market and is used as a substitute of milk. In order to see how far these powders are proper substitutes of milk, the chemical analysis of some of the powders was undertaken. So far as mineral constituents are concerned these powders are comparable with natural milk. The distribution of phosphorus compounds is similar except that pyro phosphorus and easily hydrolysable organic compounds soluble at pH 9, are absent. They might have changed over to ortho phosphorus during the process of drying. This might account for a higher value of ortho phosphorus compound in dry milk powders.

ABSTRACTS OF M.Sc. THESES

I—STUDIES IN THE CHROMONE SERIES. "TRANSFORMATION OF O-AROYLOXYACETOARONES INTO O-HYDROXY-DIAROYL METHANES AND SYNTHESSES OF FLAVONES FROM O-HYDROXYDIAROYLMETHANES." BY Mr. V. V. ULLAL, ROYAL INSTITUTE OF SCIENCE, BOMBAY.

Sodium ethoxide has been found to be an effective reagent for the transformation of o-aroxyloxyacetoarones into the corresponding o-hydroxydiaroyle methanes, which can readily be cyclised to the corresponding chromones. A variety of reagents are available for the cyclisation of o-hydroxy-diaroyle methanes; hydrogen bromide in acetic acid is satisfactory.

The use of sodium ethoxide in alcoholic solution has provided a convenient synthesis of some 2-naphthyl benzochromones, the naphthalene analogous of the flavones, through the intermediate o-hydroxy dinaphthoyle methanes. Hence through the condensation of 1-aceto-2-naphthone with α -naphthoyle chloride, β -naphthoyle chloride, 1-methoxy-2-naphthoyle chloride, 3-methoxy-2-naphthoyle chloride, in the presence of pyridine, the corresponding 2-naphthyl benzochromones have thus been synthesised. Sodium ethoxide has also been applied to effect the transformation of 2-benzoyloxy-1-acetonaphthone into benzoyl 2-hydroxy-1-naphthoyle methane, of 2-anisoyloxy-1-acetonaphthone into anisoyl 2-hydroxy-1-naphthoyle methane and of 2-cinnamoyloxy-1-acetonaphthone into cinnamoyl 2-hydroxy-1-naphthoyle methane, from which the corresponding flavones were obtained by cyclisation. Sodium ethoxide also produces rearrangement of 2-palmitoyloxy-1-acetonaphthone into palmitoyl-2-hydroxy-naphthoyle methane which has cyclised to 2-pentadecyl-5: 6-benzochromone. It has also been used effectively to transform 2-cinnamoyloxy-4-methoxy-resacetophenone into cinnamoyl 2-hydroxy-4-methoxy- benzoyl methane which was cyclised to 2-styryl-7-methoxy chromone.

V. V. U.

II—STUDIES IN CHLORALAMIDE AND CHLORAL QUINAZOLONES.

BY Mr. P. Y. KULKARNI, ROYAL INSTITUTE OF SCIENCE, BOMBAY.

In continuation of the previous work on chloralamides carried out in this Laboratory chloral has been condensed with anthranilamide and o-, m- and p-acylamino benzamides with a view to studying the effect of the substituents in the benzene nucleus on the condensation. Also along with it chloral quinazolones, obtained by condensing chloral with 2-methyl and 3-amino groups in substituted quinazolones and related compounds obtained thereby are studied.

CHLORALAMIDES

The known and unknown amides required for this work were prepared by the usual methods described in literature. The following are the newly prepared amides. 5-bromo-2-acetylamino-benzamide, 5-bromo-2-benzamino-benzamide, 3-benzamino-benzamide and 4-benzamino-benzamide. During the course of the work of the preparation of the amides the action of a few primary amines on benzoyl anthranil was incidentally studied and it was found that the benzoyl anthranil is less reactive than acetyl anthranil.

Anthranil-amide condenses with chloral to form ring closed compound, 2-trichloromethyl-1:2:3:4-tetrahydro-4-quinazolone, and the o-, m- and p-acylamino benzamides form usual chloral amide ($R \cdot CONH \cdot CH_2OH \cdot CCl_3$) with it. The o-, m- and p-acylamino groups retard the condensation of chloral with amido group as these amides condense less readily with chloral than benzamide. The o-, m- and p-acetylamino groups and as well as the o- and m-benzamino groups in acylamino benzamides have nearly the same retarding influence on chloral condensation of the amido group, but p-benzamino group has a much greater retarding influence. Unlike in salicylamide, the presence of additional negative group, in position -5 (para to 2-acylamino group) in 5-bromo-2-acylamino-benzamides, does not alter the original retarding influence of 2-acylamino group. In chloral-2-acetylamino-benzamide, unlike in chloral-salicylamide, the original orientating influence of 1-carboxyl and 2-acetyl amino group is unaltered by the presence of 1-chloralamido group.

The α -OH group in the resulting chloral amide being very active is readily acetylated, benzoylated and methylated by the usual methods. During acetylation in alkaline medium these

chloralamides give either ring closed or anhydro derivatives instead of the usual acetylated products. On treatment with phosphorus pentachloride these chloral amides gave α -chloro derivatives, which being very unstable could not be isolated. In case of chloral-2-acetyl-amino-benzamide α -ethyl and α -methyl derivatives were obtained by directly pouring the reaction mixture into ethyl and methyl alcohols respectively.

CHLORAL-QUINAZOLONES

It is wellknown that a methyl group, on a carbon atom adjacent to the nitrogen atom of a basic heterocycle as for in 2-methyl-pyridine, 2-methyl-quinoline, 4-methyl-quinoline and 2-4-dimethyl-quinoline condenses with aliphatic aldehydes to form compounds of the type $R.CH_2'CH.OH.R'$ and with aromatic aldehydes to form compounds of the type $RCH=CH.R'$. This is undoubtedly due to the activation of the methyl group by the presence of the adjacent $C=N$ linkage.

2-Methyl-4-quinazolone condenses with aromatic aldehydes giving styryl compounds, but on the other hand chloral forms with it the intermediate aldol type of condensation, *viz.*, 2- γ -trichloro- β -hydroxy-propyl-4-quinazolone (I). The β -hydroxy group in 2- γ -trichloro- β -hydroxy-propyl-4-quinazolone (I) readily eliminates as water, as on acetylation instead of giving the expected β -acetyl derivative it gives the α - β unsaturated compound (II). Also during the preparation of phenyl-hydrazone derivative of (I), the similar dehydration takes place. On treatment with strong caustic alkali the γ -trichloro-methyl group in (I) hydrolyses to carboxyl group with simultaneous elimination of a molecule of water and 4-quinazolone-2-acrylic acid (III) is obtained. It has been found that a primary aromatic amino group vigorously condenses with chloral with the formation of the compounds of the type $R.N=CH.CCl_3$, and $(RNH)_2:CH.CCl_3$ according to the molecular proportion taken and no intermediate hydroxy compound could be isolated. But -3-amino group in 2-methyl-3-amino-4-quinazolone exhibits a marked decrease in reactivity, as chloral condenses with it to give the intermediate 2-methyl-3- β -trichloro- α -hydroxy-ethylamino-4-quinazolone (IV). Chloral could not be further condensed with 2-methyl group due to the steric hindrance. On acetylation the α -hydroxy group in (IV) instead of forming the regular acetyl derivatives, eliminates similarly giving 2-methyl-3-methyl-3-trichloro-ethyl deneamino-4-quinazolone.

III—STUDIES IN COLLOIDAL SOLUTIONS. BY MR. V. C. VORA,
CHEMISTRY DEPARTMENT, WILSON COLLEGE, BOMBAY.

Part I: Colloidal zinc ferrocyanide:—In this part the changes in cataphoretic speed, stability and conductivity of zinc ferrocyanide sol, dialysed and diluted to different periods have been presented. Effect of ageing and of exposure to sun light on various properties of the colloids has also been studied.

It is found that the cataphoretic speed with progress of dialysis first increases, reaches a maximum value and then decreases while the stability continuously decreases.

In the case of sols dialysed for periods shorter than the maximum value in cataphoretic speed-dialysis curve, the cataphoretic speed, on dilution, first increases and then decreases. For sols dialysed for periods equal to or longer than the maximum in the cataphoretic speed-dialysis curve, the cataphoretic speed regularly decreases on dilution. The stability, however, for all the samples of the sol dialysed for different periods continuously decreased on dilution.

It is found that for short period dialysed sols, the cataphoretic speed first increases and then decreases on adding small increasing amounts of the electrolytes tried. For the long period dialysed sols, the cataphoretic speed continuously decreases except in the case of potassium ferrocyanide. The idea of critical potential is not supported by the results.

By allowing both the short and long period dialysed sols to age and by exposing them to sun light, the cataphoretic speed as well as stability decreases. The changes on account of exposure to light are more marked.

The conductivity of the sol regularly decreases during dialysis dilution, ageing and exposure to sun light.

The results of changes in the cataphoretic speed have been explained by considering the changes in the preferential adsorption of the similarly charged and the oppositely charged ions from the intermicellary liquid. It is found that charge and stability do not go hand in hand in all cases.

Part II: Mutual coagulation of oppositely charged colloidal solutions:—In this part results of coagulation of Prussian blue by (a) Thorium hydroxide, (b) Ceric hydroxide and (c) Ferric hydroxide and of zinc ferrocyanide by (a) Thorium hydroxide, (b) Ceric hydroxide and (c) Ferric hydroxide have been presented. Mutual coagulation of these different

pairs has been studied with reference to changes in the charge on the colloid particles during dialysis. It is observed that with progress of dialysis and by taking oppositely charged colloidal solutions of comparable purity, the zone of mutual coagulation first decreases, reaches a minimum value and then increases. The charge on the particles of the two sols, however, first increases, reaches a maximum and then decreases. The effect of various impurities present in the sol has been considered and it is observed that the effect of factors like (a) interaction between stabilising ions of the sols, (b) the mutual adsorption of colloidal particles and (c) the presence of excess of free electrolyte in the sols is not very marked. The width of the zone is mostly dependent on the electric neutralisation of the charge.

P. M. B.

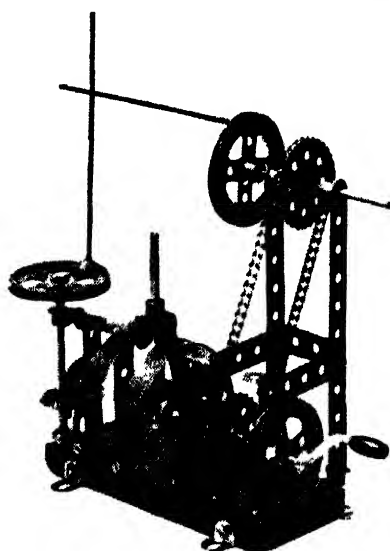
SCIENCE NOTES

COMPOSITION OF S. H. MS.

By

R. V. BARAVE

THE figure shows Pohl's apparatus made from Meccano parts to demonstrate the composition of two perpendicular



S. H. Ms. Its working is explained in "Physical Principles of Mechanics and Acoustics" by Pohl, pages 56/57 and plate III, figures 10 and 15.

The photograph shows the details of construction. The differential gear allows change of phase to be introduced in between the two S. H. Ms. while the apparatus is working. The rods

are stuck on to the wheels by pieces of wax.

The parts required are:—

Meccano part No.	Name	Quantity
2	Perforated strip	2
5	" "	3
6a	" "	3
12	Angle brackets	4

Meccano part No.	Name	Quantity
16	Axle rods ...	3
17	" "	1
19h	Crank handle ...	1
20b	Pulley wheels ...	3
25	Pinion wheel ...	1
29	Contrate wheels ...	2
30	Bevel gears ...	2
37	Nuts and Bolts $7/32"$...	27
48	Double bent strip $1\frac{1}{2}" \times \frac{1}{2}"$...	2
48a	" " " $2\frac{1}{2}" \times \frac{1}{2}"$...	5
52	Flanged plate $5\frac{1}{2}" \times 2\frac{1}{2}"$...	1
59	Collars with grub screw ...	9
63	Coupling ...	1
94	Sprocket chain ...	14"
95a	Sprocket wheel $1\frac{1}{2}"$ diameter ...	2
215	Formed slotted strips ...	4

The apparatus can be set up into rotation manually or by means of an electric motor. The results can be observed individually by watching the apparent intersection of rods against a bright background or they can be shadow-projected for large audience.

NOTES AND NEWS

SCIENCE AND WAR

THE war looms large in the mental consciousness of the world at present. The war-spirit bestrides the world. Events taking place now point to the conflagration extending and spreading beyond Europe and enveloping the whole world.

Science has come in much for criticism. Science no doubt is playing a prominent part in this war. Unfortunately there is perversion of science. Science has been prostituted "to the service of the sword and the purse". Very little has been done to prevent the perversion of science. "But the conscience of Science is clear. She offers man a rope to skip; she cannot be blamed if he chooses to hang himself with it."* Science is both a blessing and a curse. Science lacks humane and spiritual guidance. Fire is a source of warmth but it also burns. Water quenches thirst as well as suffocates. Power without wisdom is dangerous. Knowledge is power but it should be wedded to love and transmuted to wisdom. The scientist has to work in dedicated service. We see the dire effects of the use of power alone, of brute force, without the background of love and wisdom.

As rational human beings we should boldly face the issues confronting society. The present conflict seems to be a struggle between civilization and barbarism. The callous way in which the so-called civilized people behave themselves at present makes us doubt whether the present-day civilized man would be called a cultured man. A revaluation of all the values of life is most urgently needed. The present conflict seems to be due to fundamental maladjustments arising from a lack of perception of the essential values of life. A re-emphasis on the spiritual values is urgently called for. The value of the individual requires to be stressed.

* *Nature*, p. 910, 15-6-1940.

If the present war brings prominently to the forefront the question of science and its social implications and arouses among men of science full recognition of their social responsibilities, then this war will have done a useful purpose. If the present war brings about a change of heart in man and helps to bring about a new order in society broad-based upon the recognition of man as a spiritual being and upon the recognition of truth, justice and freedom, both considered as of supreme value and worthy of our highest respect and reverence, then the war will not have been fought in vain.

D. D. K.

NATIONAL PLANNING

THE work of the National Planning Committee to which reference was made in the last year's issue of this Journal, has progressed considerably and is now nearing completion. The National Planning Committee has arrived at important decisions, which are based on the reports of the various Sub-Committees, and which have been embodied in a number of resolutions. These resolutions, which are of far reaching significance and importance, will form the basis of the plan for the economic and industrial development of the country. Some of the important decisions arrived at by the N. P. C. are the following :—

1. The establishment of a heavy engineering industry for the manufacture of machinery of all kinds is essential for the industrial development and for the organisation of defence.
2. The manufacture of automobiles, etc., should be undertaken at an early date.
3. The building up of the electrical industries is considered essential.
4. The establishment of the Dye-stuff industry in India is considered necessary, and for this purpose a Dye-stuff Corporation should be formed as soon as possible, which should be either subsidised and controlled by the State or owned by it. When the factory or factories under the Corporation start operations and produce dyes of standard

quality, in sufficient quantity, the importation of dyes and intermediates should be prohibited except under license for special reasons.

5. The immediate establishment of a synthetic ammonia plant is recommended with a view to making India self-sufficient with regard to synthetic nitrogen fertilisers.
6. The indigenous drug industry should be encouraged by a protective duty on synthetic drugs imported from abroad.
7. An industry for the manufacture of explosives should be started in India.
8. All power and fuel resources of the country should be regarded as national property, and should be fully conserved, scientifically developed and utilised with a view to make power, particularly electrical power, readily available at a cheap rate for domestic and industrial use.
9. The development of a power alcohol industry should be encouraged by the State.
10. In view of the limited resources of coal which cannot be replenished, and of the indispensibility of coal for such essential industries as smelting of iron ore, production of synthetic dyes, drugs and other essential chemicals, very strict state control should be exercised on all phases of the coal industry. The use of raw coal for domestic purposes which involves waste and causes smoke nuisance should be prohibited. A sufficient quantity (3 million tons) should be distilled to produce the soft coke necessary for this purpose. The tar obtained from this process as well as from other factories should be processed to yield the road tar necessary for improving roads, ammonium sulphate for fertilisers, and the chemicals and intermediates essential for the dye and drug industries.
11. The Central Geological Survey should carry out a thorough and complete survey of the mineral resources in all parts of the country.
12. The large deposits of ores of manganese, chromium, aluminium, and other metals, which are now not being worked, should be utilised for the manufacture of the metals and their compounds. These industries are essential for the general industrialisation of the country as well as for defence.

13. Crude petroleum should be imported and subsequently refined in the country.
14. There should be a state department for industrial research, which should establish a National Chemical Laboratory, as well as such other laboratories as may be considered necessary, encourage research work in Universities, and give facilities for doing research work in different parts of the country, including grants-in-aid to co-operative research work.

R. C. S.

Table Showing M.Sc., M.Sc. (Tech.) and Ph.D. Graduates in Physics and Chemistry (1939 to 1940)
with the titles of their theses, etc.

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the Candidate worked	Name of the Institution
	M. Sc.		
Bhide, R. D.	Physics : <i>Dielectric Properties of Glycerides</i>	Prof. B. B. Deshpande	Sir P.
Desai, V. D.	<i>Some Characteristics of the Intensity Distribution in the First Positive Band System of Nitrogen in a High Temperature Source</i> ...	Dr. N. R. Tawde	R. I. Sc.
Lajmi, S. S.	<i>Further Studies in the Scattering and Transmission of Light by a Cloud of Liquid Particles</i>	Prof. G. R. Paranjpe	R. I. Sc.
Narayan-swami, R.	<i>Some Problems in Earth Magnetism and the Physics of the Atmosphere</i>	Dr. K. R. Ramanathan	Colaba Obs.
	Chemistry :		
Baljekar, P. N.	<i>Crystal Structure of some Organic Compounds</i>	Dr. Mata Prasad	R. I. Sc.
Bhagwat, N. A.	<i>The Chalkones obtained by Condensing O-anisaldehyde with Acetophenone</i>	{ Dr. R. C. Shah Dr. T. S. Wheeler }	R. I. Sc.

Chitale, R. G.	<i>Studies in the 4-aryl-coumarin-α-pyrone and 8-aryl-furo Coumarine Groups</i>	Prof. D. B. Limaye	R. I. E. I.
Dharwarkar, H. V.	<i>Studies in Chloral Hydroxy and Methyl-Benzoic Acids</i> ...	Prof. R. L. Alimchandani	K. C.
Doctor, N. S.	1. <i>Investigations on Ghee and Butter.</i> 2. <i>Studies on Ascorbic Acid (Vitamin C) and Ascorbic Acid Oxidase</i>	Dr. B. N. Banerjee	I. I. Sc.
Gharpure, D. V.	<i>A Study of the Velocity of Decomposition of some Aromatic and Aliphatic Nitriles in Homogeneous Systems</i>	Dr. D. D. Karve	F. C.
Gokhale, G. D.	<i>Constitution of Anacardic Acid</i>	Dr. R. C. Shah	R. I. Sc.
Kulkarni, P. Y.	<i>Studies in Chloral Amides and Chloral-Quinazolones</i>	{ The late Prof. N. W. Hirve } [Dr. R. C. Shah]	R. I. Sc.
Karve, R. V.	1. <i>Study of the Cinnamic Acids obtained from 5-hydroxy-4-methyl-coumarin and its derivatives.</i> 2. <i>Synthesis of 4:2'-dimethyl-coumarin-5:6 pyrone.</i> 3. <i>Study of the Bromination of 5-hydroxy-6-acetyl-4-methyl-coumarin.</i> 4. <i>Preparation of Ortho methoxy-phenylglyoxylic Acid</i>	Prof. D. B. Limaye	R. I. E. I.
Lawande, Y. V.	<i>Studies in Activated Charcoals</i>	Prof. R. N. Bhagwat	St. X.
Mavani, C. K.	<i>Studies in Coumarin Condensations</i>	Prof. R. N. Bhagwat	St. X.
Mehta, S. M.	<i>Studies in the Chemical Activity of the Halogen Derivatives of Substituted Amides of Malonic Acid</i>	Dr. R. K. Trivedi	B. C.

Table showing M.Sc., M.Sc. (Tech.) and Ph.D. Graduates in Physics and Chemistry (1939 to 1940)
with the titles of their theses, etc.—contd.

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the Candidate worked	Name of the Institution
Nabar, J. A.	<i>Studies in the Adsorption of Naphthol Dyes by Cotton Fibre</i> ...	{ Dr. B. N. Desai } { Dr. S. C. Devadatt }	W. C.
Nhavi, N. G.	<i>Absorption of Phosphates from the Intestines and some Factors which Influence it</i> ...		Gor.
Parikh, H. P.	<i>Study of Chemical Activity of the Chloro Compounds of the substituted Amides of the Cyan-acetic Ester</i> ...	Dr. V. N. Patwardhan	B. C.
Patwardhan, W. D.	<i>1. Syntheses in the Furo-coumarane Group. 2. Synthesis in the Coumarin-γ-pyrone Group. 3. Action of Alcohols on β-4-methoxy Phenyl Glutacetyl Acetic Acid</i> ...	Dr. R. K. Trivedi	
Rao, H. N.	<i>Studies in Heterogeneous Reactions in Solution...</i> ...	Prof. D. B. Limaye	R. I. E. I.
Sane, L. Y.	<i>Studies in Chloral Amides</i> ...	Dr. Mata Prasad	R. I. Sc.
Sathe, P. R.	<i>1. Action of Diethylsulphate on 2. Acetyl-resorsin and Oxidation of Diethylether of 2-acetyl-resorsin</i> ...	{ Late Prof. N. W. Hirve } { Dr. R. C. Shah }	R. I. Sc.
		Prof. D. B. Limaye	R. I. E. I.

Savkar, G. S.	<i>Synthesis of Keto Butyric Acids with Hydroxy Phenyl or Methoxy Phenyl Groups as Substituents in α and γ Positions</i> ...	{ Dr. K. S. Nargund } { Prof. K. V. Bokil }	G. C.
Setlur, A. A.	<i>Studies in Benzoic Acid Derivatives</i> ...	Prof. R. N. Bhagwat	St. X.
Shejwalkar, B. G.	<i>Studies in Thorium Arsenate Gels. (Studies in Gelation)</i> ...	Dr. Mata Prasad	R. I. Sc.
Shenoi, R. B.	<i>Enolisation of Diaroyl Methanes</i> ...	{ Dr. T. S. Wheeler } { Dr. R. C. Shah }	R. I. Sc.
Shroff, H. P.	<i>Synthesis of Alkyl-α-naphthols—The Synthesis of 2-propyl-2-butyl- and 2-isobutyl-α-naphthols</i> ...	Prof. R. N. Bhagwat	St. X.
Telang, M. S.	<i>Kinetics of the Reaction between Potassium per Sulphate and the Alkyl Iodides.</i>	Prof. R. N. Bhagwat	St. X.
Vakil, (Miss) V. M.	<i>Y-substitution in Resorcinol Derivatives</i> ...	Prof. R. N. Bhagwat	St. X.
Virkar, V. V.	<i>Naphthyl Chromones with Particular Reference to Naphthalene Ring</i> ...	{ Dr. T. S. Wheeler } { Dr. R. C. Shah }	R. I. Sc.
Vora, V. C.	<i>Studies in the Colloidal Solutions</i> ...	Dr. S. C. Devadatta	W. C.
Waravdekar, V. S.	<i>Synthesis of Hydroxy-Ketones containing Long Chain Alkyl Radicals</i>	Prof. R. N. Bhagwat	St. X.
M.Sc. (Tech.)			
Dalsal, N. M.	<i>Cracking of Vegetable Oils</i> ...	Dr. T. N. Mehta	Dept. of Chemical Technology

Table showing M.Sc., M.Sc. (Tech.) and Ph.D. Graduates in Physics and Chemistry (1939 to 1940)
with the titles of their theses, etc.—concl.

Name of the Candidate	Subject of the Thesis	Name of the Professor under whom the Candidate worked	Name of the Institution
Kanibkar, K. R.	<i>A Study in the Properties of Modified Starches</i>	Mr. G. B. Jambuserwala	Dep t. of Chemical Technology
Kudva, K. G.	<i>Investigation of the Preparation and Properties of Coloured Cements.</i>	Dr. N. R. Damle	Do.
Parikh, V. A.	<i>Drying of Milk by Spraying</i>	Dr. N. R. Damle	Do.
Shirolkar, G. V.	<i>Textile Auxiliary Agents containing Acid Amide Group</i> Ph.D.	Dr. K. Venkataraman	Do.
Davar, D. J.	Physics : <i>Solvent Effect in Dipole Moment Measurements</i>	Prof. G. R. Paranjpe	R. I. Sc.
Deshpande, P. Y.	<i>A Study of Dielectric Properties of Fatty Acids and their Compounds</i>	Prof. G. R. Paranjpe	R. I. Sc.
Dhatmatti, S. S.	<i>Magnetic Properties of Selenium and Tellurium and some of their Compounds</i>	Prof. G. R. Paranjpe	R. I. Sc.

Chemistry :

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C. T.

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Chitre, R. G.

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Ferreira,
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G. C.

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N. L.

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Dr. K. S. Nargund

{ G. C. & }
{ Sir P. }

Sethna, S. M.

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Dr. R. C. Shah

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§ *Publications of the Punjab Historical Society*, Lahore.

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Truimasik, Shree Forbes Gujarathi Sabha Mandir, 365, Girgaon, opp. Lamington Road, Bombay, 4.

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MARCH 1941

Vol. IX (New Series), Part 5.



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[BIOLOGICAL SCIENCES, INCLUDING MEDICINE: No. 9]

VOL. IX (New Series)

MARCH 1941

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NOTICE

This issue completes Volume IX (New Series) of the Journal. The Title Page and Index will be sent in due course.

According to the revised scheme, the two Science issues of the Journal will be combined, and each issue will consist of two Sections: (A) Physical Sciences, including Mathematics, and (B) Biological Sciences, including Medicine. The issues will be published in November and March, as usual.

Manager

COMPOUNDS OF PHOSPHORUS IN MILK POWDERS

By

DR. B. N. ACHARYA, M.Sc., Ph.D.,

AND

DR. S. C. DEVADATTA, D.Sc. (Edin.),

Chemistry Laboratories, Wilson College, Bombay 7

MILK in the form of dry powders is available in the market and is used as a substitute of milk. In order to see how far these powders are proper substitutes of milk, chemical analysis of some of the powders was undertaken. Milk powders A and B of well known standard firms were selected.

Though some work has been done on the general composition of milk powders yet the type of work which was carried on with fresh milk is lacking. It has been reported that the ash of milk powders has been analysed for phosphorus and calcium.¹ The amount of phosphorus pentoxide (P_2O_5) is stated to be 1.8 per cent and calcium oxide 1.5 per cent of the powders.

A further attempt has been made by Lampitt, Bushill and Filmer² for the estimation of phosphorus, calcium and magnesium. They have subdivided the acid soluble phosphorus compounds in milk powders into organic and inorganic. Dialyses of milk powders was carried out by them by subjecting the solutions of milk powders to static methods.

Acharya and Devadatta³ have shown that phosphorus in the Bombay buffalo milk exists in at least seven different forms. An attempt has been made now to investigate the milk powders for these Phosphorus compounds. They⁴ have also discussed the distribution of phosphorus, calcium and

1. Davies, Chemistry of Milk, p. 427, 1936 Edn.

2. Lampitt, Bushill and Filmer Biochem., J., 31, 1861, 1937.

3. Acharya and Devdatta, J. Ind. Acad. Sci., X, 221, 1939.

4. Ibid. X, 229, 1939.

magnesium salts in the fresh Bombay buffalo milk. Similarly a study of the milk powders for insoluble salts was thought desirable. 20 per cent solution of the milk powders was selected for comparison with the buffalo milk as the percentage of total solids in the Bombay buffalo milk and the former were found to be approximately the same.

Composition of milk and of the milk powders A and B
expressed in percentage of milk or of solution

		Bombay buffalo milk	20 per cent solution of A	20 per cent solution of B
Fats	...	9.00	3.74	4.00
Proteins	...	4.00	5.51	5.17
Carbo-hydrates	...	4.80	9.48	9.66
Ash	..	0.80	1.26	1.66
Total Solids	...	18.60	19.99	20.49

From the above table it can be seen that nearly 60 per cent of the fat present in milk has been removed in the preparation of milk powder. It may be noted that the milk powders contain 30 per cent more of proteins and twice as much of carbo-hydrates as are normally present in the fresh milk. Therefore the composition of buffalo milk and that of 20 per cent solution of the milk powder are not quite comparable. Moreover, this concentration chosen on the basis of total solids, should at least form a homogeneous mixture; but this was not found to be the case. It is possible to bring the 20 per cent solution of milk powder into a homogeneous colloidal condition by applying heat. For finding out different types of phosphorus compounds it is necessary to prepare a homogeneous mixture in the cold, *i.e.*, at the room temperature. Heat is likely to have some effect on phosphorus compounds. Therefore various concentrations of milk powders were tried and it was found that eight per cent solution possesses a homogeneous colloidal consistency. In this connection it may be mentioned that Lampit, Bushill and Filmer (*loc. cit.*) prepared nine per cent solution. Since the physical appearance of eight per cent milk powder solution was homogeneous, it was used in the investigation presented here.

EXPERIMENTAL

The details of the procedure for the estimation of the phosphorus compounds, calcium and magnesium carried out in this investigation are essentially the same as those given by Acharya and Devadatta (*loc. cit.*). Every figure recorded in all the tables represents the average of six determinations estimated directly. Wherever possible the difference or the total of two estimations was used merely as a check for values obtained by direct estimations.

RESULTS AND DISCUSSION

TABLE I

Composition of milk powders A and B
(grams per 100 grams of powder)

	A	B
Moisture	2.70	2.50
Fat	18.20	19.46
Proteins	26.80	25.20
Carbo-hydrates	46.10	47.10
Mineral matters	6.20	5.66

TABLE II

Analysis of milk powders: Phosphorus, Calcium and Magnesium in milk powders in acid and water soluble and insoluble fractions
(mg. per 100 grams of milk powders)

	A			B		
	Phosphorus	Calcium	Magnesium	Phosphorus	Calcium	Magnesium
(1) Milk powder	784	876	96.08	724	814	82.20
(2) Acid insoluble portion	172.8	292	6.06	160.2	271.8	5.22
(3) Acid soluble	611.40	586	90.02	564.10	544.6	76.98
(4) Undialysable (water insoluble)	403.86	524.5	6.06	372.30	487.3	6.00
(5) Dialysable (water soluble)	379.20	350.6	90.40	350.00	325.30	76.26
(6) Undialysed (acid insoluble)	87.00	218.0	...	81.00	202.60	...
(7) Undialysed (acid soluble)	316.80	306.0	...	392.20	285.0	...

- N.B.*—(1) The sum of either 2 and 3 or 4 and 5 is equal to 1, *i.e.*, total phosphorus, calcium or magnesium in milk powder.
- (2) The water insoluble portion (4) is subdivided again into acid soluble (7) and acid insoluble (6), *i.e.*, the sum of 5, 6 and 7 is equal to 1.

TABLE III

Analysis of acid insoluble fraction of milk powders into
lipoid phosphorus and casein phosphorus

(Phosphorus in mg. per 100 grams of milk powder)

	A	B
Acid insoluble phosphorus	172.80	160.20 (c.f. Table II, 2)
Casein phosphorus	157.94	144.88
Lipoid phosphorus	14.86	15.32

TABLE IV

Analysis of acid soluble, water soluble and (water insoluble but)
acid soluble fractions into organic and inorganic phosphorus
compounds (Table II, 2, 5 and 7)

(Phosphorus in mg. per 100 grams of milk powders)

	A			B		
	Organic	Inorganic		Organic	Inorganic	
		Ortho	Pyro		Ortho	Pyro
Acid soluble ...	85.45	526.2	Nil	80.02	486.00	Nil
Dialysable ...	61.02	318.18	...	56.34	294.20	...
Undialysable acid soluble ...	21.64	293.90	...	20.10	271.80	...

TABLE V

Organic phosphorus (acid soluble) further divided into soluble and insoluble in barium hydroxide at pH = 9
(mg. of phosphorus per 100 grams of milk powders)

		A			B		
		Soluble in Ba (OH) ₂		Insoluble in Ba (OH) ₂	Soluble in Ba (OH) ₂		Insoluble in Ba (OH) ₂
		Hydrolysable	Non-Hydrolysable		Hydrolysable	Non-Hydrolysable	
Acid soluble	...	Nil	24.6	60.96	Nil	22.90	56.72
Dialysable	...	Nil	17.6	43.46	Nil	16.40	40.94
Undialysable acid soluble	...	Nil	6.4	14.76	Nil	5.96	13.95

TABLE VI

Changes taking place in the concentrations of different types of (acid soluble) phosphorus compounds of fresh milk on ageing
(Phosphorus in mg. per 100 c. c. of milk)

Time in hours	Fraction insoluble in Ba (OH) ₂			Fraction soluble in Ba (OH) ₂		
	Inorganic		Organic	Organic P		
	Ortho P	Pyro P	Non-Hyd P	Non-Hyd P	Easily Hyd P	
1	46.90	15.28	10.52	5.40	10.20	Total phosphorus in milk = 110.63 mg.
1	52.48	13.64	10.52	5.40	7.20	
2	65.30	11.00	9.64	6.40	3.68	Total acid soluble phosphorus = 86.10 mg.
3	65.86	7.42	9.30	5.20	Nil	
4	69.86	3.42	9.00	5.10	Nil	
5	70.56	2.22	8.64	5.10	Nil	
6	72.96	Nil	8.50	5.10	Nil	
7	75.46	Nil	8.50	5.10	Nil	
8	75.46	Nil	8.50	5.10	Nil	

N.B.—Pyrophosphate disappears from milk after it is kept for 6 hours; similarly easily hydrolysable soluble in Ba(OH)₂ fraction disappears after 2 hours.

TABLE VII

Changes taking place in the amount of pyrophosphate when the acid soluble portion of milk is subjected to ageing

(Phosphorus in mg. per 100 c.c. of milk)

Time in minutes	Ortho phosphorus	Pyro phosphorus	Total phosphorus	Total A. S. P.
30	43.89	13.76	105.83	82.90
60	48.96	7.96		
90	53.86	3.42		
120	57.32	Nil		

N.B.—In the presence of acid, pyrophosphate changes into the ortho condition within two hours.

TABLE VIII

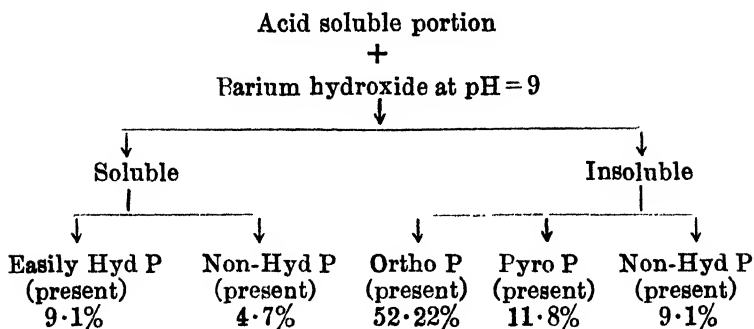
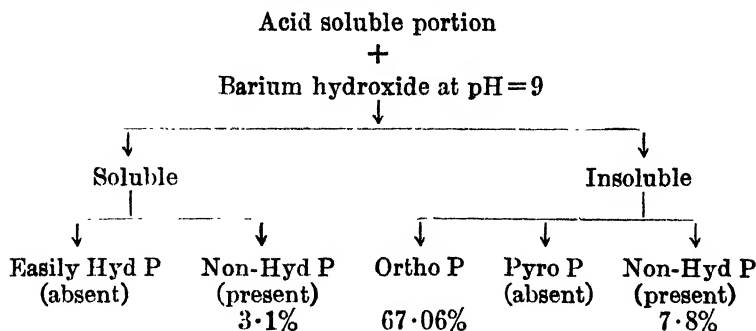
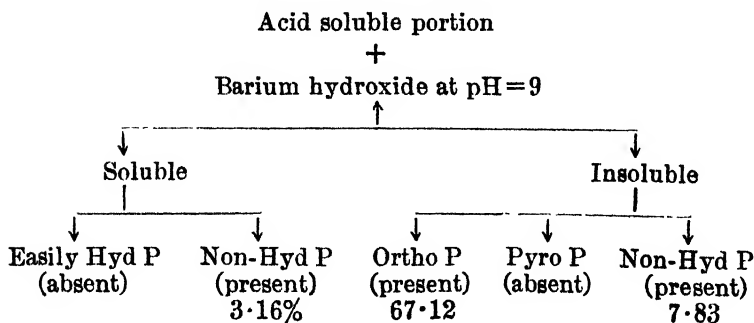
Effect of heat on the pyrophosphate content of milk with progress of time

(Milk heated on a boiling water bath)

(Concentrations of phosphorus in mg. per 100 c.c. of milk)

Time in hours	Ortho phosphorus	Pyro phosphorus	Total acid soluble phosphorus
$\frac{1}{2}$	41.29	12.20	78.98
1	46.69	6.80	
2	49.86	3.66	
3	50.20	3.21	
$3\frac{1}{2}$	51.16	Nil	
4	53.63	Nil	

N.B.—Pyrophosphate is destroyed on heating milk at about 98°C for $3\frac{1}{2}$ hours.

A. Analysis of fresh milk**B. Analysis of milk powder A****C. Analysis of milk powder B**

In Table 1 are recorded the composition of milk powders A and B. Since the two powders were found to be similar in composition, for convenience, the results of one of the powders namely A are taken here for discussion. The results of B being similar to that of A, the same discussion holds good for B as well.

In Table 2 are given the amounts of phosphorus, calcium and magnesium in various fractions of milk powders. It is seen that 784 mg. of phosphorus, 876 mg. of calcium and 96.08 mg. of magnesium are present in 100 grams of A. Out of 784 mg. of phosphorus 611.4 mg., *i.e.*, 78 per cent, is acid soluble and the remaining 172.8 mg.—*i.e.*, 22 per cent—acid insoluble. The acid soluble phosphorus of the Bombay buffalo milk is about 73.6 per cent of the total phosphorus and 26.4 per cent being acid insoluble *i.e.*, 86.87 mg. and 31.33 mg. respectively per 100 c.c. of milk. Acharya and Devadatta (*loc. cit.*).

Acid soluble organic phosphorus compounds :—Tables 4 and 5 deal with the amounts of organic and inorganic phosphorus contents of the two milk powders studied. It is seen that in A, 85.45 mg. or 10.9 per cent of the total phosphorus is in organic condition and 526.2 mg., *i.e.*, 67.06 per cent, in inorganic condition. In the Bombay buffalo milk the amount of acid soluble organic and inorganic phosphorus compounds constitute 24.27 per cent and 64.02 per cent respectively. The percentage of organic phosphorus in the acid soluble portion of milk powder is less than that in the corresponding portion of fresh milk (*c.f.* p. 7), in other words, some organic phosphorus compound has changed over into the inorganic variety in the process of conversion of milk into powder. This point is discussed and the type of organic compound responsible for this fall in organic phosphorus is indicated.

It was shown by Acharya and Devadatta (*loc. cit.*) that when trichloroacetic acid extract of milk is treated with barium hydroxide at $\text{pH}=9$, three types of organic phosphorus compounds could be estimated—(1) Soluble in barium hydroxide at $\text{pH}=9$ which could be estimated by the direct application of Brigg's method, (2) Soluble in barium hydroxide at $\text{pH}=9$ which could only be estimated after oxidation and hydrolysis and (3) Insoluble in barium hydroxide which could be estimated after oxidation and hydrolysis. These three types of organic phosphorus compounds were looked for in the milk powders studied. The diagrammatic scheme above (p. 7) gives the amounts of different types of phosphorus compounds in the Bombay buffalo milk and in the milk powders.

Taking organic phosphorus into consideration it may be noted that the easily hydrolysable organic phosphorus compound soluble in barium hydroxide at $\text{pH}=9$, which could be estimated by the direct application of Brigg's method was not present at all in the milk powders whereas in milk it is present to the extent

of 9.1 per cent of total phosphorus. The amounts of the other two types of organic phosphorus compounds (2) and (3) both being estimated after oxidation and hydrolysis are given in table 5; they are respectively 24.6 mg. (or 3.1 per cent) and 60.96 mg. (or 7.8 per cent) in A. In the Bombay buffalo milk they are respectively 4.7 and 9.1 per cent. It is clear therefore that the milk powder contains 10.9 per cent of the total phosphorus in the acid soluble organic form whereas the Bombay buffalo milk has 22.9 per cent.

Inorganic phosphorus compounds:—The inorganic phosphorus compounds of milk exist in two different forms—(1) the ortho and (2) the pyro, respectively being 52.88 and 11.8 per cent of total phosphorus. Acharya and Devadatta (loc. cit.). When these were looked for in the milk powders no trace of pyrophosphate could be seen. The higher percentage of the ortho phosphorus in milk powders, *i.e.*, 67 per cent is obviously from two sources, *viz.*, (a) the easily hydrolysable organic phosphorus compound and (b) the pyrophosphate. The next problem is to see by what treatment or reactions and at what stage these compounds are converted into the inorganic ortho form. For this purpose, freshly drawn milk was allowed to stand for a number of hours and the amounts of different types of phosphorus compounds were estimated as usual: the results are given in Table 6. It is seen from the table that the easily hydrolysable phosphorus changes into inorganic ortho form on simply keeping the milk for three hours; similarly the pyrophosphorus compound is also changed to ortho variety during the course of six hours. It is observed, on the other hand, that if the trichloroacetic acid extract of milk is kept for two hours the pyrophosphorus is converted into the ortho condition (refer Table 7). It may also be inferred from Table 8 that the pyrophosphate is completely destroyed on heating the milk continuously for three hours in boiling water bath. Easily hydrolysable organic phosphorus compound changes to ortho variety when milk is similarly treated.

Acid insoluble phosphorus compounds in milk powders:—The acid insoluble phosphorus compounds mainly consist of casein phosphorus, and lipid phosphorus; (refer Table 3) 14.86 mg. of lipid phosphorus constitutes about 2 per cent of the total phosphorus of the milk powder whereas the Bombay buffalo milk contains 4.05 mg. per 100 c. c. of milk, constituting 3.5 per cent of the total phosphorus. Also it can be seen from Table 3 that 20% of the total phosphorus in milk powder is due

to casein phosphorus. The percentage of casein phosphorus agrees very well with that of the Bombay buffalo milk.

Acid soluble constituents.—No useful purpose is served by speculating on the nature of water soluble constituents in milk. But, if the water soluble contents are differentiated from the acid soluble, an insight into those which are soluble in acid only is possible.

Water soluble constituents were separated from the milk powder by dialysing 8 per cent solution in parchment bags for 30 hours against distilled water. The results are given in Table 2. It may be noted that the amounts of phosphorus, calcium and magnesium which are dialysable are respectively 379.2 mg., 350.6 mg. and 90.4 mg. per 100 grams. Similarly the amounts of phosphorus and calcium which do not pass through parchment paper are 403.86 mg. and 524.5 mg. respectively per 100 grams. Magnesium is found in traces in the undialysed fraction. Analysis of the acid extract of undialysed part was carried out as usual and the amounts of phosphorus, calcium and magnesium present in 100 grams of milk powder soluble in acid only, are respectively 316.8 mg., 306 mg. and traces. Now the sum total of water soluble and water insoluble but acid soluble contents, phosphorus 696.0 mg. and Calcium 656.6 mg., is more than that of the values got by the direct treatment of the powders with acid, *i.e.*, phosphorus 611.4 mg. and calcium 586 mg. If we assume that the constituents soluble in water are also soluble in acid we have to explain for this increase in the amounts of phosphorus, calcium and magnesium in water + acid soluble portions over that of acid extract. This excess is due partly to the fact that casein which had adsorbed calcium and magnesium ions on coming in contact with water becomes partly soluble, *i.e.*, acid insoluble portion becomes water soluble. This point is discussed already elsewhere⁴.

The next point is to see the possible insoluble compounds that may go to form from the amount of phosphorus, calcium, and magnesium available in the undialysable acid soluble fraction. They are tricalcium phosphate and magnesium phosphate. It can be seen (from Table 2) that 316.8 mg. of phosphorus and 306 mg. of calcium are undialysable but soluble in acid. Assuming that this above calcium is present as tricalcium phosphate, then out of 316.8 mg. of phosphorus only 163.5 mg. are utilized. The remaining 153.3 mg. phosphorus may be due to the organic phosphorus discussed already. Therefore about 50 per cent of water insoluble acid soluble phosphorus

goes to the formation of insoluble salts and the remaining is in the organic condition.

SUMMARY

1. The study of phosphorus compounds in milk powders reveals that except for the absence of pyro and easily hydrolysable organic variety, the nature and the amounts of the rest are similar to those met with in fresh milk. The former are converted into the ortho form which is to be expected.
2. Acid soluble inorganic phosphorus is in ortho condition and the organic is in two forms—soluble and insoluble in barium hydroxide at pH 9.
3. Acid insoluble phosphorus compounds are lipoid and casein with calcium and magnesium adsorbed ; part of the latter becomes soluble on dialysis.
4. Water insoluble constituents consist of tricalcium and magnesium phosphates and organic phosphorus.

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POWDERY MILDEW OF THE MANGO

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INTRODUCTION

POWDERY mildew of the mango, which has been shown by Wagle (1928) to be the cause of shedding of mango flowers and fruits in the Ratnagiri District, was first recorded in the Province of Bombay in 1917-18 by Ajrekar (1918), who considered it to be a species of *Oidium*. Later, the name *Erysiphe cichoracearum* D.C. was proposed in the Annual Report of the Plant Pathologist to the Government of Bombay for the year 1923-24 (1925), but no description of the morphological characters of the fungus was published. Wagle (1928) was the first worker in Bombay to give a brief account of the conidial phase of the fungus, but followed "the Mycological authorities at Poona" in referring the fungus to *E. cichoracearum*. As he has given no description of the perfect stage, it is doubtful whether he had seen the perithecia of the fungus. Wagle also makes no mention of haustoria which, in this fungus, are saccate or lobed—a characteristic not found in *E. cichoracearum*.

As early as 1914 Berthet (1914) had applied the name *Oidium mangiferae* to a mildew on mango in Brazil, and, since the perithecial stage of this fungus has not yet been discovered, Berthet's name should be preferred. As the description given by Berthet is very brief, a detailed account of the fungus as occurring in this Province is given below.

MORPHOLOGICAL AND PHYSIOLOGICAL CHARACTERISTICS

The fungus causing mildew on mango produces on the inflorescence and its stalk, and the young fruit, superficial, septate mycelium, which ramifies over the surface of the host, forming a white, dense coating of much branched hyphae, ranging in diameter from 4.1 to $8.2\ \mu$. The hyphae in contact with the host form on the under surface haustoria, which arise as slender tubes and pierce the cuticle and cell walls; these tubes then swell up inside the epidermal cells, forming sac-like structures (Fig. 1, A). Appressoria also develop on the under side of the hyphae and fix the latter firmly to the epidermal wall (Fig. 1, E). Sometimes two appressoria may arise at the same point on the opposite sides of a hypha (Fig. 1, E).

From the superficial mycelium numerous branches arise as conidiophores with two to more basal cells (Fig. 1, F). The conidiophores measure from 64 to $163\ \mu$, are unbranched and bear on their ends unicellular, hyaline, elliptical conidia having truncated ends. These spores are produced in basipetal succession but are sometimes seen in chains of two, as the conidia easily fall off when mature. Since the conidia greatly vary in size, 400 of these were measured and grouped into a series of measurement classes. It will be seen from Table I that widely differing lengths of conidia are encountered, but a vast majority of them fall in the classes between 33 and $42.9\ \mu$. The range of variation in width, however, is not large since more than 80 per cent of conidia fall between 18 and $21.9\ \mu$. (Fig. 1, C).

TABLE I

Summarised measurements of conidia of *Oidium mangiferae*

Classes in μ	Length	Classes in μ	Width
	Number of conidia in 400		Number of conidia in 400
25 to 26.9	2	16 to 17.9	38
27 to 28.9	2	18 to 19.9	94
29 to 30.9	15	20 to 21.9	237
31 to 32.9	16	22 to 23.9	31
33 to 34.9	42		
35 to 36.9	44		
37 to 38.9	110		
39 to 40.9	105		
41 to 42.9	32		
43 to 44.9	22		
45 to 46.9	8		
47 to 48.9	1		

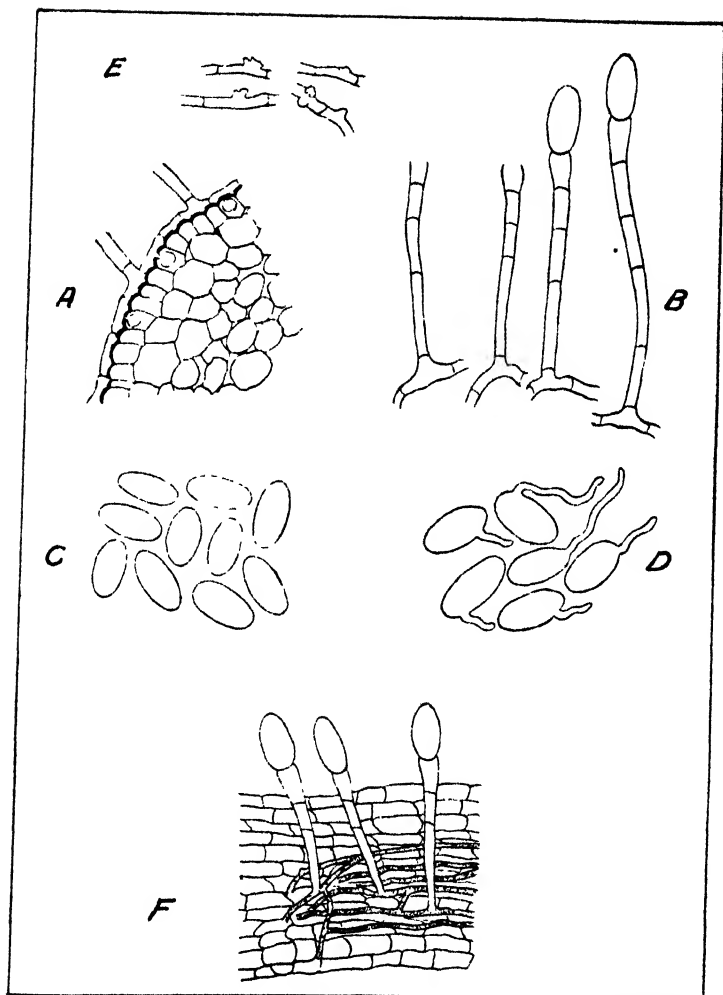


Fig. 1.

A. Transverse section of an infected flower stalk showing haustoria on the under side of the superficial hyphae. **B.** Conidiophores bearing ovate or elliptical conidia. **C.** Conidia showing the range of shapes and sizes. **D.** Germinating conidia. **E.** Appressoria on superficial hyphae. **F.** Portion of flower stalk showing septate mycelium, forming a tangled web of hyphae; conidiophores and conidia.

Fresh conidia freely germinate by the protrusion of a germ-tube (Fig. 1, D). Germination of the conidia was studied in water cultures at various temperatures. The figures in Table II are the averages obtained from 12 tests and represent the percentages of germination at the end of 24 hours.

TABLE II
Effect of temperature on germination of conidia of
Oidium mangiferae

Temperature (°C)	Per cent of germination
7.5	0
9	trace
11.5	11.7
13.5	14.2
18	17.1
20	35.7
22	44.7
25	30.0
30	trace
32.5	0

The conidia do not germinate in water at 7.5°C., but there is some measurable germination at 9°. With further rise in temperature germination increases and is at its optimum at 22°. It then falls off sharply and is completely suppressed at 32.5°. The low percentages of germination obtained at different temperatures were due to the growth of saprophytic organisms in water cultures as the conidia are usually coated with sugary secretions of mango hoppers, which are associated with the attack of mildew on the inflorescence.

The favourable temperatures for germination of conidia are generally experienced along the coast in the cold season when the mildew is quite destructive.

DESCRIPTION

The following is the description of the conidial phase of *Oidium mangiferae* Berthet on *Mangifera indica* L. :—

Mycelium superficial, branched, hyaline, septate, 4.1 to 8.2 μ in diameter, forming a white, dense coating on inflorescence and its stalk, and the young fruit. haustoria saccate. Conidiophores erect, simple, with two to more basal cells, ranging from 64 to 163 μ in length. Conidia unicellular, hyaline, elliptical, extremes varying from 25 to 48.9 μ in length and 16 to 23.9 μ in width, mostly 33 to 42.9 \times 18 to 21.9 μ , borne singly or rarely in chains of two, germinating by a tube.

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THE INTRICACIES OF ECTOPIC PREGNANCY

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IN spite of our advances in the knowledge of Gynaecological diseases and their treatment, there are yet many unsolved problems in this realm of medicine; and Ectopic pregnancy, with its innumerable intricacies, is certainly one of them, the solution of which tries the experience and the skill of the gynaecologist.

I have preferred the term Ectopic pregnancy because it has reference to any abnormal implantation of the ovum outside the uterus. It covers gestations which may be Ectopic without being extrauterine; such as interstitial, gestation in an adenomyometous crypt of the uterine cavity leading to intramural pregnancy, gestation in a rudimentary horn of a bicornuate uterus and in a didelphus uterus. Such anomalies of gestation, in particular, give rise to many intricacies in their diagnosis and treatment.

THE INCIDENCE

It is difficult to ascertain the prevalence of Ectopic pregnancy in Bombay. The condition is really an obstetric anomaly, but it is most often met with in the gynaecological department, both because of its frank resemblance to pelvic disease and because of errors in diagnosis, which are estimated to occur in from 15% to 40% of the cases. This large percentage of error is, I believe, due to the intricacies of Ectopic pregnancy. Moreover, many patients do not seek allopathic advice but prefer the Vaydias and Hakims. The incidence of Ectopic pregnancy in my practice has been one in every 300 consecutive gynaecological operations. The increasing incidence of Ectopic pregnancy is relative rather than actual, and it is to be explained by increasing accuracy in diagnosis.

THE ETIOLOGY

The etiology of Ectopic pregnancy is still in a nebulous state. Although the causes are believed to include any condition which mechanically interferes with the downward passage of the ovum, especially, congenital anomalies of the tube, previous inflammatory disease; previous pelvic surgery; abnormalities of the ovum; hormonal deficiency and reversion to type; many a time none of these can be found at the operation, nor is there any clinical evidence of disturbance of the menstrual and genital function in the past history of the patient.

SYMPTOMATOLOGY AND DIAGNOSIS

Whatever the views on the causation of the Ectopic pregnancy may be, there is no doubt that the manifestation of the disease varies in different individuals and the symptoms presented depend on the site of implantation of the ovum, its behaviour and the reaction of the tissues of the individual. Even cases with the same site of implantation do not have the same termination. One may rupture within two or six weeks and lead to a classical Ectopic syndrome, another may abort or rupture and subsequently develop in a new site and yet another may grow for five or six months and the foetus die and be retained as a litopodium, or the gestation may go to term, to be mistaken for a post mature complicated labour.

A classical Ectopic syndrome needs no comment. A gynaecologist of experience can detect it through the phone, but it is the subacute case that gives rise to intricacies that surprise the gynaecologist the most. It is indeed astonishing how a "leaker" can go on for a long time without the clinical syndrome, with a gradual increase of the abdominal swelling, without any alteration of the pulse rate, or any acute pain or any clear symptoms of internal bleeding. How often do we not find such cases, who when admitted to the hospital, leave the hospital in a day or two against advice and travel miles and miles from hospital to hospital or to their homes, perhaps to return to the hospital, after some time, with increased abdominal pain and vaginal bleeding or presenting an acute abdominal emergency? Theoretically, it appears incompatible that such cases could carry on in this manner without any fatal rupture, but in practice we find that many of them do so.

The symptomatology of an Ectopic pregnancy is often intricate or intriguing. In the early stages of the gestation, the

symptoms and findings are notoriously indefinite, and even after rupture the classic syndrome is not always present and to say in Kelly's words, "the most typical thing about the disease is that it is atypical".

The patient either does not know that she is ill or she considers herself normally pregnant. The first symptoms may be those of early uterine pregnancy, with the discomfort perhaps slightly more pronounced, or there may be no symptoms at all. According to Rushmore, the symptoms may be: first, those of pregnancy; second, those of disturbed pregnancy; third, those of tubal disturbances; and fourth, those of peritoneal disturbances apart from the tubes.¹

The history of the patient is most important, especially the previous tubal pregnancies, previous pelvic operations, previous inflammatory disease or absolute or relative sterility. Even most important is the type of the last menstrual period. This the patient usually ignores. The fact that the period has occurred at all convinces her that pregnancy cannot exist and it is almost impossible to ascertain from her the fact that the flow was scanty, intermittent, clotted or in some way different from her usual periods. Pain is invariably absent before rupture. The abdominal examination reveals little or nothing and the pelvic examination, if is not entirely negative, is only characteristic of any thing but an apparently normal pregnancy.

The first sign of impending rupture is spotting or irregular bleeding of a peculiar brownish colour, which is usually ignored because it is considered to be evidence of delayed menstruation. Pelvic pain appears next, but only in the small classic group is of a sudden, piercing type, associated with collapse and shock, which is pathognomonic of tragic cases and which is unfortunately considered to be characteristic of all cases. More often the pain is moderate with repeated exacerbations and remissions and repeated small haemorrhages are more frequent than the massive variety.²

The period of amenorrhoea is very variable and instead of two to six weeks amenorrhoea it is not very rare to meet with a period of two to four months amenorrhoea before the classic signs are manifest and the symptoms presented by the patient may then be mistaken for those of disturbed uterine pregnancy.

To demonstrate some of these points, I shall recall a type of case I met some time ago. Mrs. X.³, aged 29, was admitted to my hospital, for intermittent uterine bleeding and pain in June.

The history : Her childhood and puberty were uneventful. She menstruated at 13 ; her periods were regular, lasting four days each month. She was married at the age of 26. She had a spontaneous abortion, at two months, a year after her marriage. Since the abortion, her general health was good. Her last period was in February. On admission there was no bleeding, but she stated that she bled off and on and sometimes profusely, from April to May. She had consulted several gynaecologists, because of the intermittent bleeding and pain. Some suspected vesicular mole and others Ectopic pregnancy. Worried with the diagnosis, she travelled over 1500 miles by rail and arrived at Bombay early in June. She looked a bit pale. Her general condition was good. On examination nothing abnormal was detected in any of the systems, but a cystic swelling could be felt just at the level of the symphysis pubis. The swelling was tender on palpation. On vaginal palpation the cervix was soft and was displaced to the left. The uterus was retroflexed and the fundus uteri displaced to the right; its shape and size could not be clearly defined. A cystic swelling filled the left half of the pelvic cavity, continuous with the left border of the uterus. It was fluctuating and tender. The D. P. was tender and attempts to lift the fundus uteri from the right fornix caused pain.

Friedman's test was strongly positive, but negative for vesicular mole. It was decided to keep the patient under observation and watch the progress of the swelling and the symptoms. The total blood count showed R. B. C. 3,500,000, W. B. C. 12,000 and Hb. 60 per cent.

After some days of observation, no apparent change was found in the swelling nor was there any bleeding, but the tenderness in the D. P., on vaginal palpation, had increased. The possibility of an angular or interstitial pregnancy was now advanced and expectant treatment advocated; but the patient was anxious to know the exact diagnosis; moreover, she was working in a district where expert treatment, in case of any emergency, was not available. She was also anxious to get to work and herself pressed for an exploratory laparotomy. It was undertaken with much reluctance, and the following were the findings :—

(1) The swelling was uterine. The uterus was pregnant, but did not present the usual congested appearance. It was pale.

(2) The uterus was retroflexed, the lower anterior wall was prominent and the left half was distended. Fig. 1.

(3) While lifting up the fundus uteri from the pelvic cavity, thin bands of adhesions were torn off.

(4) When the fundus uteri was brought up to the laparotomy wound it began to contract and disclosed its true arcuate shape. The size of the uterus corresponded to the period of the gestation. Fig. 2. The appendages were normal; a small corpus luteum was seen on the right ovary.

After confirming the diagnosis of an angular pregnancy the abdomen was closed. Convalescence was uneventful. Fig. 3 is the radiograph, taken on the 18th day after the operation, showing the foetus on the right side. The patient went to term and delivered spontaneously of a baby boy.

It would be interesting to note here that the deflection of the cervix uteri to the left and of the fundus uteri to the right, the soft tender fluctuating swelling in the left half of the pelvic cavity, a swelling that would not contract, and the history of intermittent bleeding after a period of amenorrhoea, led to the error in the diagnosis of the case.

Gestation in the isthmus or the interstitial portion of the tube is most deceptive. The symptoms and signs presented are atypical and the encroachment of the swelling on the fundus uteri confounds the physical signs found on examination. The following case illustrates :—

Mrs. Y.⁴, a 5th para, aged 44, was admitted to my hospital on the 13th of April, complaining of a vague hypogastric pain and vaginal bleeding for three weeks. She stated that she was $2\frac{1}{2}$ months pregnant. She appeared worried and complained now and again of a feeling of fainting and epigastric oppression. She did not appear anaemic. Her pulse was 130, respiration 30 and temp. 98.

The present history: After two and half months amenorrhoea, she felt a colicky pain on the right iliac fossa, which was followed by slight vaginal bleeding. The pain soon subsided after some treatment, but the bleeding, though slight, was still going on. General examination revealed no organic disease. On vaginal examination, the uterus was found normally anteflexed and anteverted but somewhat pushed to the right and presented the physical signs of uterine pregnancy of about two to three months, but was tender to palpation and its contour

could not be minutely defined. The tenderness was marked on the left side of the fundus uteri. The left fornix was normal, but tender. There was no tenderness or any swelling felt in the right fornix.

The past history was negative. She never suffered from any acute disease since her marriage, her general health was good. She was fairly well built. Her menstruation was normal and regular. She had four normal deliveries. The third was of twins—a boy and a girl. Her fourth child was $4\frac{1}{2}$ years old. The last three confinements were in my hospital and uneventful.

On the face of the history and the physical findings, she was kept under observation, with a provisional diagnosis of threatened abortion and given uterine sedatives. On the third day the bleeding was practically the same—scanty and reddish brown. I had to leave Bombay, on official work, on the 16th of April and returned on the 1st of May. During my absence the vaginal bleeding was scanty and intermittent. The pulse kept between 110 and 120 and the patient complained of occasional sensation of fainting, but, no pain. On the 30th of April she passed a uterine cast and the bleeding stopped. During my absence, she was examined by my assistant who thought that the uterus was increasing in size, but did not find any swelling in the fornices. When I examined the patient on the 2nd of May, I found the swelling rising to the umbilicus and was deflected towards the right. The right fornix, though short, was free from any swelling or fluid. The pelvic swelling felt definitely cystic. The pulse was 115 and there was no acute pain nor any bleeding per vagina. Since admission, the temperature rose to 100 on the 3rd day and had been ranging between 97 and 100 on many evenings.

From the beginning I had the suspicion of an Ectopic pregnancy, although no clear clinical evidence was available, and as I found, on my return, that the swelling was fast increasing, I decided to operate.

On opening the abdomen, blood clots were found underneath the peritoneum. When these were cleared, a bluish swelling, the size of a foetal head, was seen occupying the left pelvic quadrant and rising above the pelvic brim. Fresh blood clots were seen on either side of the swelling. Attempts to lift the swelling ended in rupture and free fluid (liq. amnii) flew out and in its midst a live foetus of about four months development was found twisting and turning. The uterine body was deflected to the right and the interstitial portion of the left tube had

ruptured. The placenta was in the rent of the uterus and on the ruptured wall on the outer side of the sac. Fig. 4 shows the condition found at the operation and Fig. 5, the specimen removed. After removing the sac, attempts were made to close the rent in the uterus, but the bleeding could not be controlled and a subtotal hysterectomy was performed. The recovery was uneventful.

The abdominal syndrome in an Ectopic is many a time misleading. The peritoneal reaction to haemorrhage varies in different individuals. Ordinarily free intra-abdominal haemorrhage gives rise to the classic signs with collapse and shock, but yet, one comes across cases of free leakage of blood into the abdominal cavity without any manifestation of rise in the pulse or any sign of acute abdominal emergency.

Mrs. Z., a Hindu, 3rd para, aged 25, was admitted to my wards at the K. E. M. Hospital, complaining of severe pain on the right side of the abdomen and vaginal bleeding. She stated that she felt at first a colic on the right side of the abdomen, which was followed by vaginal bleeding. The colic was followed by pain which had grown worse for the last week. The bleeding was slight but bright red. Her pulse was 100, respiration 20 and temp. 98. She did not appear anaemic.

The abdomen was prominent and a somewhat cystic swelling could be palpated rising from the pelvis to above the level of the umbilicus, but deflected towards the right hypochondrium. The upper pole of the swelling extended to the right costal margin and was tender. On P. V. the uterus was anteflexed and somewhat enlarged and soft. The left fornix was empty, but the right was full and an elongated mass could be felt extending upwards and continuous with the abdominal swelling. It was tender.

Past history: She menstruated at 14, regularly every month, 3 to 4 days. She was married in childhood. She had two spontaneous labours and the puerperia were normal. The last child was three years old. No history of any acute illness could be obtained. She stated that she had a period of four months amenorrhoea before the colicky pain and vaginal bleeding and that she thought she was pregnant.

On the next day of admission the swelling increased in size, but there was not much pain. The vaginal bleeding was scanty. Though the history of the patient and the physical signs did not warrant an Ectopic gestation, yet as the uterine enlargement did

not correspond with the period of amenorrhoea and the Friedman's test was positive, I decided to operate. On opening the abdomen free haemorrhage was met with, but the site of the bleeding could not be detected. It appeared to be in the right iliac fossa. The incision was rapidly extended upwards and on retraction a cystic mass, the size of a large plum, surrounded by blood clots, was detected. Attempts to lift the mass from its base caused its rupture and liquor amnii intermixed with blood oozed out freely, in the midst of which live twin foetuses, of about four months gestation, were found wriggling about. The active bleeding was outside the sac and was caused by the rupture of adventitious vessels in the right iliac fossa. Fig. 6 illustrates the condition found at the operation. The placenta was implanted partly on the caecum and partly on the posterior abdominal wall.

Evidently it was a tubal abortion which had found a secondary implantation. The sac and the hypertrophied right tube were removed. The bleeding on the placental site had to be controlled by ligatures and gauze packing. The patient later on developed faecal fistula, but eventually recovered.

It is surprising, indeed, that with so much intra-abdominal bleeding there was no clinical evidence of internal haemorrhage, before the operation.

Considering the caliber of the Fallopian Tube, its anatomical structure, the scanty decidual reaction and the trophoblastic invasion, it is but natural that a tubal gestation should rupture or abort sooner or later.

The ability of the tube to accommodate the foetus to term, without rupture, is doubted by most gynaecologists, yet one comes across, in one's life-time, a case or more of advanced tubal gestation, without rupture, with a confusing history and intricate clinical and physical signs.

Mrs. D.⁵, aged 27, was admitted to my ward, at the K. E. M. Hospital, complaining of acute abdominal pain and vaginal bleeding.

The history: The patient stated that a year and half ago, after a period of six months amenorrhoea, she had a profuse period which lasted for nine days. This was followed by amenorrhoea for the next two months, after which she bled for ten days. Then after another period of two months' amenorrhoea, she had a severe attack of pain on the left side of the abdomen, which

was followed by bleeding that lasted for about a month. The pain, however, subsided after a fortnight, but she noticed that the left side of the abdomen was now rather prominent. This, she said, had been gradually increasing since and that for the last three months she had blood stained discharge. The pain had now reappeared with intensity and she was passing blood clots per vagina. The pain and the bleeding had brought her to the hospital for treatment.

The past history : Menstruation commenced at the age of 13 and lasted for 8 to 9 days, each month. She married in childhood. She had two full term deliveries and two abortions in between the deliveries. The last delivery was two years ago and spontaneous.

On admission she appeared anxious, anaemic and emaciated. Her pulse was 88, temp. 98·5 and respiration 24. The lower abdominal wall was rigid, the rigidity being marked on the left side.

On vaginal palpation, the cervix was soft and patulous. The uterine body was deflected to the right, anteflexed and slightly enlarged. The left fornix was prominent and distinct pulsation was felt in this fornix. A well defined doughy mass, the size of a pumlow, filled the pelvic cavity. The mass could be moved from side to side, but could not be lifted off the pelvis. It was tender on palpation.

As the pain and bleeding persisted, I decided to operate. On opening the abdomen, the tumour was found covered by the omentum, which presented unusually distended vessels. The omentum was firmly adherent to the tumour, in some parts. At one particular spot, when the omentum was separated from the tumour, quick haemorrhage followed from the tumour, which had to be temporised by pressing a sponge on the bleeding surface. The operation was simple. The technique adopted was that of Salpingo-oophorectomy for a pedunculated ovarian cystoma.

Even after removal, the tumour appeared to be an ovarian cystoma, but for its colour, which was reddish brown in some parts. On careful examination of the tumour, a flattened ovary was detected on its posterior surface, which gave the clue of it being a tubal distention. Fig 7. On section of the tumour, after fixing it, the wall was found very much thickened, and a fresh blood clot was found at the site of the placenta (retroplacental haematoma). The placental tissue did not appear macerated or

disintegrated. A flattened foetus, resembling a sole fish, was curled round the placenta and the blood clots. As a matter of fact, it was first mistaken for the thickened wall of the tumour. The development of the foetus appeared to be that of about six and half months. Fig. 8.

The striking points in this case are :—(1) that the foetus developed in the tube for over six months, (2) that the death of the foetus and its subsequent papyrations changes did not cause abortion or rupture, (3) that the placental tissue was active and caused retroperitoneal haemorrhage, which led to pain, (4) that in spite of uterine bleeding on several occasions during one full year, the Fallopian tube did not abort or rupture, and (5) that the foetus was retained in the tube, after its death, for nearly one year, being subject to pressure sufficient enough to cause its flattening.

Tortion of the Fallopian tube, although rare, may mimic the ectopic syndrome; and still rare is the torsion or entanglement of the Hydatid Morgagni with the Kobelt's tubule, with the same results. Both these conditions can only be diagnosed or detected after opening the abdomen. To wit: Mrs. A., a multipara, aged 25, was admitted to my wards at the K. E. M. Hospital for acute abdominal pain and slight vaginal bleeding. She was treated at the out-patient department for retroflexion and a Hodges pessary was applied five days before the admission.

Her past history was uneventful. Her periods were regular but painful since the birth of the last child, five years ago. Her labours and puerperia were normal. She was well built and fairly nourished.

On admission, the pessary was removed and the patient put to bed and the usual mist. Viburnum co. prescribed. But in spite of rest and sedatives the pain increased in intensity. On P. V. the uterus was found retroflexed and the fundus uteri soft, slightly enlarged and tender. The left fornix was tender and some fluid appeared to be present in the D. P., which was also tender. As the condition of the patient would not improve, it was decided to operate.

On opening the abdomen free serous fluid was found in the D. P. and, to my great surprise, the pedicles of the Hydatid Morgagni and of the Kobelt's tubule were found twisted. Both were haemorrhagic. The appendages were healthy but the uterus was retroflexed and congested. The twisted pedicles were tied and the two little currant looking bodies were excised. A

modified Gilliam's suspension completed the operation. Fig. 9 illustrates the condition found at the operation.

Developmental⁶ uterine anomaly is often the source of error in diagnosis of pregnancy. Anomalies of number, shape and partition, such as: didelphic uterus (uterus duplex separatus cum vagina separata), double uterus with one cervix (uterus duplex unicollis), and septate or bilocular uterus (uterus septus duplex), are the common atavism of nature met with. These are rarely suspected or detected before conception and lead to much confusion during the first quarter of pregnancy.

During my 30 years of obstetrico-gynaecological practice I have come across 14 cases of such anomalies and the majority of these were detected in the gynaecological department, some pregnant and others non-pregnant. My very first case⁷, which put me later on the lookout for such anomalies, was very instructive.

Mrs. B., aged 25, was admitted to my hospital at 10 p.m. on the 14th of February....., bleeding rather profusely and with acute abdominal pain, pronounced on the left side, abdomen tender, tense, pulse 120, temp. 97, and looking pale and anxious.

Present history: She had been bleeding very slightly on and off since the 8th of February. The abdominal pains began with the bleeding and had, after returning from a drive, increased in severity since that evening. Did not menstruate in December and January. In October last she had pains in the left pelvic quadrant and was bleeding off and on for several days. She was then admitted to a hospital and kept under observation. There was at first suspicion of an extra-uterine gestation, but later on, after 21 days' stay in the hospital, she was curetted and the uterine cavity douched. She kept well until the 8th of February, but for pelvic pains and discomfort.

Previous history: Menstruation regular in frequency and duration, four to five days. General health good. Married seven years. First full term delivery in 1919—prolonged labour, forceps—still birth—weight 6 pounds; spontaneous abortion at six months in 1921—foetus 3 pounds, born alive. Third full term delivery 1923 (two years ago), Breech, normal.

On examination: Abdominal wall tense and tender. A distinct swelling fills the left pelvic half and rises about one and a half inches above the iliac crest, irregular in contour and nodular to the feel.

The vagina is full of blood clots, cervix slightly softer and granular to the feel. The uterus cannot be clearly defined. A cystic swelling rises from the left fornix and extends about one and a half inches above the iliac crest, pyriform and tender.

Diagnosis: Ruptured Ectopic pregnancy in the left broad ligament.

Treatment: As there was no immediate urgency, the patient was put to bed, to be carefully watched, and a small morphia injection ordered, to be repeated if required, and the operation fixed for the next morning. At 2 a.m. the pains were severe and the swelling was more central and seemed to contract with each pain. An enema was ordered. The enema was followed by spontaneous delivery of a macerated foetus of about 23 weeks gestation.

I examined her on the 3rd day, as she still complained of pains on the left side of the pelvis, and a swelling could be felt below the left iliac crest. The cervix felt wide and granular, the uterus could not be clearly defined, it was centrally situated and retroverted. The fundus uteri was slightly enlarged, a doughy mass was felt rising from the left fornix into the left broad ligament, somewhat pyriform and tender to the touch. On examining the vagina with a speculum, the cervix was found patent and full of round granulations, and an old tear was apparent on the left side.

As she complained of pain on the left side I decided to operate, and on the eleventh day after abortion I performed the operation.

On opening the abdomen, to my great surprise, I found two uteruses joined together at the level of the internal os and opening into one common cervical canal. Both were fully developed, the left (puerperal) being about one-third larger than the central. As the relatives of the patient objected to hysterectomy, I removed both Fallopian tubes and closed the abdomen. Fig. 10 illustrates the findings at the operation.

Comment: In October she was probably threatening to abort. The central uterus was curetted, while the left was threatening to abort. Pregnancy in the left tube was not disturbed by the curettage of the central. The physical signs on admission and the true account of the previous trouble and operation led to a possible diagnosis of an ectopic pregnancy. The three previous pregnancies probably took place in the central uterus.

Accidental perforation of a non-pregnant uterus by instruments or of a pregnant uterus by a abortionist may lead to active haemorrhage and the symptoms presented may be mistaken for those of an Ectopic pregnancy. The history given by the patient is invariably misleading. I have had several such experiences. I shall mention one of them.

Mrs. C., aged 24, a nulipara, was brought to my office, for consultation, complaining of acute hypogastric pain and vaginal bleeding for five days. She looked anxious and pale.

On examination, the abdomen was tense and tender, pulse 130, respiration 30 and temp. 97. On P. V. the uterine body could not be defined, but a boggy tender mass was felt filling the pelvic cavity.

The history: She stated that she was treated by a doctor, for three weeks, for menstrual irregularities and sterility; that the doctor was applying some medicine to the womb twice a week and that since the last application, five days ago, she felt severe pain in the lower abdomen and started bleeding. The bleeding was scanty but bright red. Her periods were irregular and her last period was six weeks ago.

As the patient could not afford private treatment, she was immediately sent to the K. E. M. Hospital with a provisional diagnosis of a ruptured Ectopic, to be operated on the next day, but meanwhile to be carefully watched for emergency.

On opening the abdomen, on the next day, the pelvic cavity was full of blood clots. On clearing the clots, fresh blood was seen oozing out but the exact site of bleeding could not be ascertained. The uterus was retroflexed, congested and the appendages were normal. On lifting up the fundus uteri, a small rent was found on its anterior wall, a little above the utero vesical peritoneal reflexion, from which blood oozed out. The rent was closed by a few catgut sutures, the uterus suspended and the abdomen closed after instilling 20 c.c. of electragol into the pelvic cavity. The recovery was uneventful. A year and half after, the patient was admitted for confinement and this was spontaneous.

In this case the doctor had probably attempted to correct a retroflexed uterus by means of a sound and had unconsciously caused the perforation.

Much stress on the parity and the period of sterility of the patient is also a source of error in diagnosis of an Ectopic.

During October last I operated on two ruptured Ectopics ; one was a 4th para who had a premature labour seven months before admission to the Hospital. Her previous pregnancies, labours and puerperia were uneventful. She had gone only ten days over her periods ; and the other was a young woman of 20, who was only two months married. This case was rather misleading. She gave no history of amenorrhoea, but of intermittent bleeding and colicky pain for a month.

On vaginal examination, a soft, tender, small mass was felt in the left fornix and a solid mass, the size of an orange, in the right fornix. The D. P. was very tender—uterus anteverted and antefixed, but its size and contour could not be clearly defined.

As the pain increased in intensity and also the size of the swelling, a ruptured Ectopic pregnancy was diagnosed. On opening the abdomen, the left mass was found to be a ruptured tubal gestation, the rent on the tube was on its middle 3rd, and the right solid mass was a Dermoid cyst of the ovary.

Such and other swellings in the pelvis do, indeed, increase the difficulties of diagnosis of Ectopic pregnancy.

Various signs and laboratory tests are considered to be pathognomic of Ectopic pregnancy ; to mention a few, *viz.* :—

1. Cullen' umbilical sign.—I have not been fortunate to detect this sign, although I have opened many abdomens filled with blood.

2. Shoulder pain.—This sign is met with in some cases, but cannot be relied upon as it is often met with in other conditions.

3. Aschheim Zondeck, Freidman's, Broha's and the Hogben tests are reliable adjuncts in differentiating Ectopic pregnancy from inflammatory conditions in the pelvis or in the upper abdomen, but they are of little help in differentiating a uterine pregnancy or an interstitial pregnancy from a tubal pregnancy.

4. Ferrar has pointed out the value of repeated blood examinations, by the same pathologist, on the ground that the marked decrease in red cells and the high fluctuating white cell count which accompany Ectopic pregnancy are in marked contrast to the unchanging haemoglobin and the steady high leucocytosis of inflammatory lesion. I have found this test of great value.

5. Vaginal puncture is advocated by some gynaecologists, if a fluctuating swelling is found in D. P., and aspiration of

blood establishes the diagnosis, but the puncture is of not much value as a diagnostic aid until after intraperitoneal rupture, nor is it devoid of risk.

6. A hysterosalpingography is a valuable asset provided that uterine pregnancy can be safely excluded. Moreover the possibility of a simultaneous intra-uterine and a extra-uterine gestation must be remembered.

7. Colpo-diaphanoscopy has been suggested as an additional test; but the lighting phenomenon varies with the density or opacity of the fluid contents of the pelvis, and cannot always be relied upon.

Although these tests are very valuable when positive or present, in confirming the diagnosis of an Ectopic pregnancy, their absence is not always dependable, but is likely to misguide the gynaecologist who puts much trust in them.

TREATMENT

Ordinarily, the treatment of an Ectopic pregnancy is simple enough. The rationale of the treatment should be the same as of surgical haemorrhage—"to cut down and tie the bleeding points".

It has been my practice to operate as soon as this anomaly of conception is diagnosed or the sign of internal haemorrhage is confirmed. Prompt operation has given me the best results. Agility and skill are the essential requirements for a prompt operation. Even in the very acute case, one with trained tactile sense and thorough knowledge of pelvic anatomy, can plunge into a pool of blood and although he cannot see the pelvic anatomy he can control the haemorrhage by clamping the bleeding tube, much faster than his less agile colleague. Hirst⁶ is perhaps right when he says that many of the gynaecologists who advocate delayed operations in shock are the slow surgeons with an academically correct technique, while those with a more rapid technique take the opposite view because of their ability, as Murphy puts it, "to get in quick and get out quicker". For the essence of safety in most of these cases is operation within the shortest possible period. When active bleeding has been controlled, and the patient's condition is good, time may be taken to complete the abdominal toilet, but in the tragic case with massive haemorrhage not a moment should be lost. In such cases, it is my practice to quickly remove the clots, leave the fresh free blood in the peritoneal cavity and pour a pint of

sterile normal saline, at body temperature in the abdominal cavity and close the abdomen; it is quickly absorbed and it supplies the necessary fluids.

I prefer to remove the Fallopian tube *in toto*. It is invariably found damaged and conservative operations often lead to subsequent trouble, including the possibility of future Ectopic pregnancy, but should the other tube be diseased or removed previously then I have resource to conservatism.

It is difficult to lay down a routine technique for the treatment of Ectopic pregnancy. Cases, there will be, which, on opening the abdomen, will present problems for immediate solution, which will depend on the knowledge of macroscopic pathology and the surgical wisdom of the operator. Dense adhesions may be met with and the liberation of the appendages becomes then an arduous task. The opposite tube may be found so congested, angry and thickened that it is difficult to differentiate the changes from those of inflammatory lesions. In such cases it is my practice to pass a stout silk worm gut into the tube, to ensure its patency, and when found patent, to leave the tube alone, instil 20 c. c. of electragol into the pelvic cavity and close the abdomen. The results have been encouraging.

The control of the haemorrhage from the raw and damaged surfaces often tries the patience of the operator and may compel him to pack the pelvic cavity with gauze or to perform a hysterectomy, especially in interstitial and intramural pregnancies.

The ovary is some times involved in the sac or buried in blood clots and is likely to be removed in the hurry along with the tube. To avoid such accident it is wise to control the bleeding by applying light clamps, one on the proximal end of the tube and the other on the meso-salpinx, turn out the clots or the sac, search for the ovary, locate it and then perform solpinctomy.

In advanced Ectopic pregnancies the removal of an active placenta and the control of haemorrhage from the placental site is a matter that calls for serious consideration. It is the situation of the placenta that determines the amount of haemorrhage rather than its active circulation. When the implantation encroaches upon the intestines or other viscera, gentle handling and care are needed to remove the placenta piecemeal and ligate the bleeding points whenever possible to avoid fistulae.

On several occasions I had to advocate gauze plugging as a last resource.

The choice of anaesthesia is important. Spinal anaesthesia is unfortunately out of question in a desanguinated patient or in a patient with a low blood pressure. Ether is contra-indicated only by pulmonary disease but otherwise is the satisfactory anaesthetic because a peritoneal cavity full of blood is exceedingly difficult to relax promptly and fully and because the relaxation which is achieved by ether permits the necessary manipulation within a minimum period of time. In desanguinated patients I prefer local anaesthesia re-enforced by a few whiffs of A, C, E mixture.

MORTALITY

The mortality in operations for Ectopic pregnancy varies with different operators and it is said to be about 2 to 7 per cent. I remember having lost one case only. She was curetted twice, for intermittent bleeding in some hospitals and was admitted to my Hospital with high temperature and repeated rigors. She was frightfully septic and died 24 hours after the operation.

SUMMARY

1. The causation of Ectopic pregnancy still remains one of the unsolved problems in gynaecology and until this problem is solved prophylaxis of Ectopic pregnancy will be a matter of speculation.

2. Some of the intricacies met with in the diagnosis and treatment of Ectopic pregnancy, during a period of 30 years of Obstetrico-Gynaecological practice have been described and illustrated.

3. The utility of some methods of diagnosis is mentioned and the obvious conclusion is that the clinical sense of the gynaecologist is more valuable than all the available signs and tests.

4. Treatment is simple in most of the cases. Early diagnosis and prompt and skilful operation is the panacea for the reduction of the mortality of this anomaly of pregnancy.

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Diagram showing the condition found on opening the abdomen—
Note the retroflexed uterus with its prominent lower anterior wall and its distended left half.

Fig. 1

Diagram showing the arcuate shape of the uterus and its size, after it was brought to its normal position—
Note the Corpus Luteum on the right ovary, in the inset.

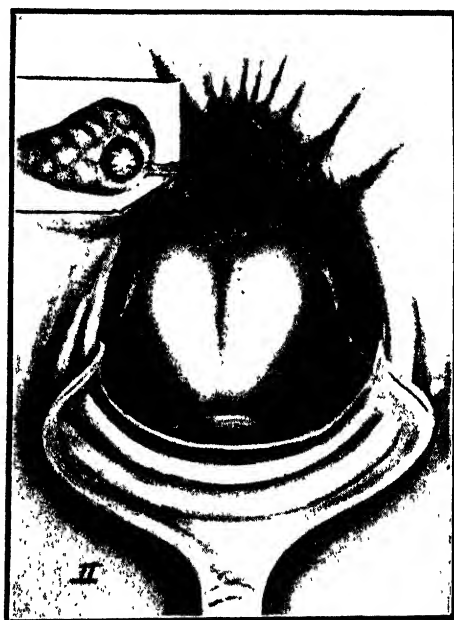
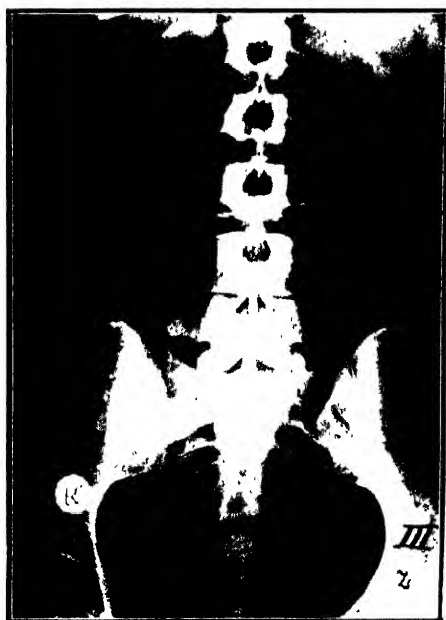


Fig. 2



Radiograph taken on the 18th day of the operation, showing foetal bones on the right side.

Fig 3



Diagram to illustrate the condition found on opening the abdominal cavity. Note the free blood and the blood clots, the site of rupture, the rent in the uterus, the attachment of the placenta, the amniotic sac and the foetus.

Fig. 4



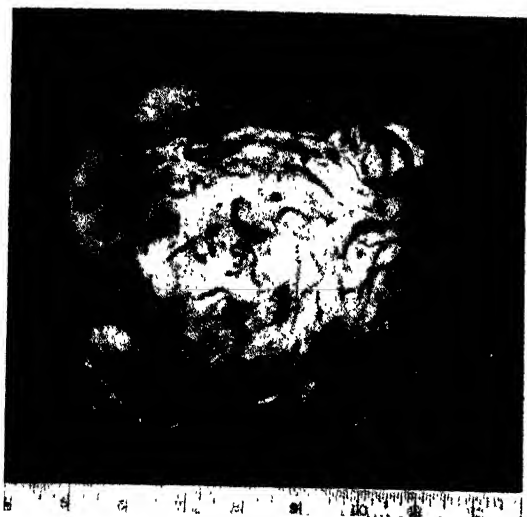
Fig. 5

Photograph of the specimen removed. Note the site of rupture, the attachment of the placenta and the size of the foetus.



Fig. 6

Diagram showing free blood in the abdominal cavity, the implantation of the placenta, the amniotic sac and the foetuses as found on opening the abdominal cavity.



Photograph of the tumour, after the operation. Note its colour and the distended vessels on its surface.

Fig. 7

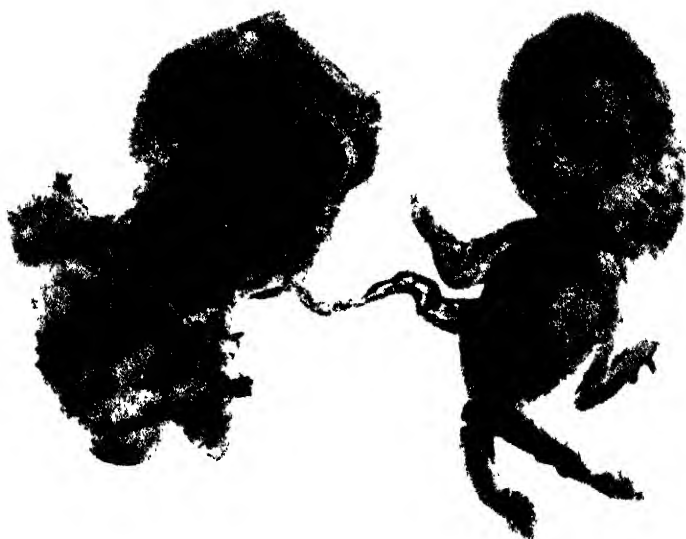


Fig. 8

Photograph of the opened specimen showing the unrolled placenta and the foetus. Note the flattening in the foetus.

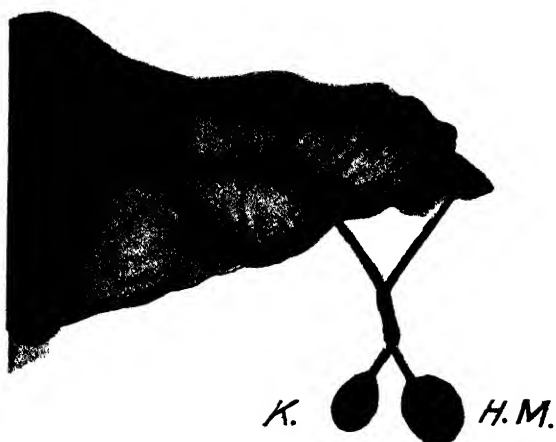


Fig. 9

Diagram illustrating the entanglement of the pedicles of the Kobelt's Tubule and the Hydatid Morgagni. Note the strangulation of the two bodies.

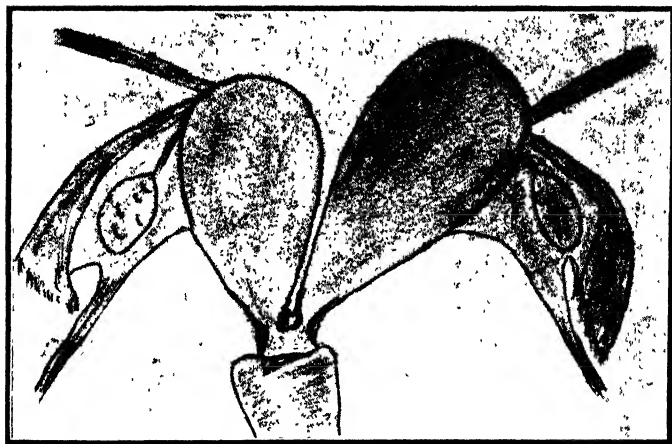


Fig. 10

Diagram of the uterus Duplex unicolis. Note the size of the nonpuerperal and the puerperal uterus.

THE TRICEPS BRACHII IN DOG, MONKEY AND MAN

By

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THE monkey dissected was *Semnopithecus Entellus*, or what is locally known as the Hanuman monkey. It belongs to the suborder Anthropoidea and the family Cercopithecidae.

Only the outstanding features of the muscle will be described, and the differences will be discussed.

In all these three animals the muscle has three heads of origin, called the long, the lateral and the medial heads. The whole muscle is disposed in two strata. The long and the lateral heads form the more superficial or the posterior (caudal) stratum. The medial head forms the deeper or anterior (cranial) stratum.

The long head.—In man it takes origin by a flat tendon from the lateral one inch of the axillary border of scapula. In the monkey and the dog the origin is from the ventral part (corresponding to the lateral part in man) of the axillary border as in man, but it is more extensive. It is about three inches wide and occupies more than half of the axillary border of the scapula.

The lateral head.—In all the three animals it takes origin by short tendinous fibres from the lateral aspect of the posterior surface of the humerus, in its upper one-third.

In the monkey this head also takes origin from the posterior aspect of the lateral intermuscular septum.

In the dog the lateral head also takes origin by an aponeurosis from the cranial (anterior) border of the humerus. This part of the origin is continuous above with the above mentioned origin. The whole origin of the lateral head lies directly superficial to the brachialis.

The medial head.—In man and the monkey the medial head takes origin from the posterior (caudal) surface of the humerus.

In man it also takes origin from the posterior surfaces of the medial and the lateral intermuscular septa.

In the monkey there is no origin from the intermuscular septa. The posterior surface of the lateral intermuscular septum gives origin to the lateral head, while the medial intermuscular septum is absent in this animal.

In the dog the medial head is almost completely separated into two parts; a more medial one, and a more lateral one called the accessory head. The more medial part takes origin by a flat aponeurotic tendon, about one inch long, from the crista tuberculi minoris (corresponding to the medial lip of the bicipital groove in man), at about the junction of the upper one-third and the lower two-third of the humerus. The origin lies directly cranial (anterior) to the insertion of the coracobrachialis. The more lateral (accessory) head takes origin from the posterior aspect of the surgical neck of the humerus.

In man and the dog the ulnar nerve lies between the medial intermuscular septum and the medial head, while in the monkey it lies on the caudal (posterior) surface of the medial part of the medial head, between the medial and the long heads.

Insertion of the triceps.—In man it is inserted by a broad aponeurotic tendon into the posterior part of the proximal surface of the olecranon of the ulna and into the deep fascia of the forearm on each side of the olecranon. Occasionally a small part of the medial head is inserted into the posterior part of the capsule of the elbow joint. This part is called the subanconeus.

The long and the lateral heads are attached to the borders of the aponeurotic tendon and the fibres of the medial head are attached to the deep (anterior) surface of this tendon, a bursa intervening between the main tendon of insertion and the posterior surface of the capsule of the joint.

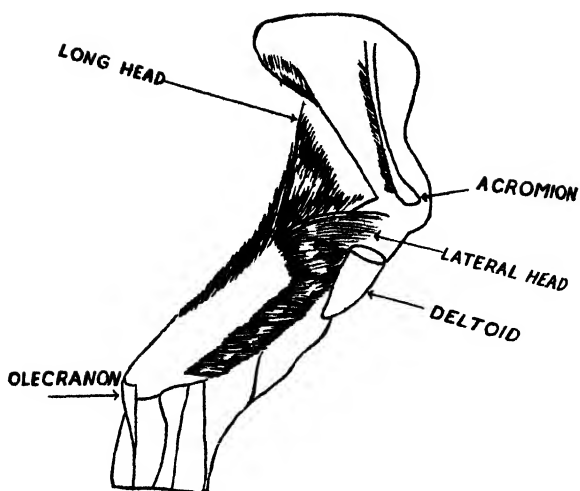


Fig. 1. Long and lateral heads of Triceps in monkey as seen from the lateral aspect.

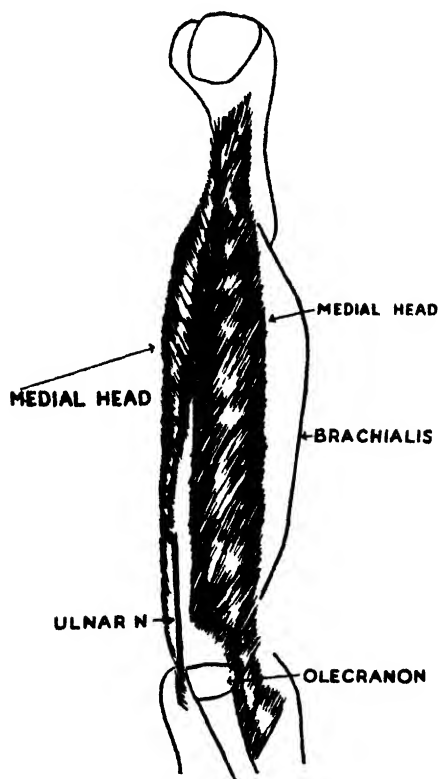


Fig. 2. Medial head of the Triceps in monkey.

In the dog the insertion is almost the same as in man.

In the monkey the insertion differs slightly from that of man. The long and the lateral heads are inserted into the posterior (caudal) part of the proximal surface of the olecranon of the ulna by a flat tendon. The medial head remains almost completely separate from the long and the lateral heads and is inserted independently by a short tendon into the anterior part of the proximal surface of the olecranon. The lower and the lateral part of the medial head gives indication of slight separation from the rest of the medial head. This part is triangular in shape and its deeper fibres are inserted into the posterior part of the capsule of the elbow joint.

Between the insertion of the long and the lateral heads more posteriorly (caudally) and the insertion of the medial head more anteriorly (cranially) there is a mucous bursa on the superior surface of the olecranon, separating the two tendons of insertion almost completely, except at the lateral end where there is slight indication of fusion.

From the description given above the questions arise:—

1. Why should the origin of the long head be so extensive in the lower animals ?
2. Why should the medial head of the triceps in this monkey be almost quite separate from the rest of the triceps mass, and what is the significance of the ulnar nerve lying posterior to the medial head ?

While considering these points it is not possible to go in the evolution of the triceps. Neither this monkey nor the dog is in direct line of descent of man, nor can it be said with justification that the evolution of the superior extremity has progressed further in man than in these animals. On the contrary there are reasons to believe that the superior extremity has remained in a more primitive stage in man than in the quadruped mammals. Under these circumstances it is only possible to consider these points from the point of view of function and comparative anatomy.

The more extensive origin of the long head of the triceps in the lower animals as compared to man, is due to the greater functional demand to which the long head is subjected in these animals.

In man the long head of the triceps has practically no power of producing extension at the shoulder joint. The most important action of the long head on the shoulder joint is to help the other muscles to maintain the head of the humerus in its position. Thus the long head together with the long head of the biceps, coracobrachialis and the deltoid does not allow the head of the humerus to be pulled down by the force of gravity.

In this monkey and the dog the long axis of the scapula is directed almost directly dorsoventrally, while in man it is directed mediolaterally and forwards (ventrally). To be more exact the long axis of the scapula in this monkey forms an angle of about 80° with the coronal plane while in man the scapula is situated at an angle of about 30° to the coronal plane. This is mostly due to the shape of the thoracic cavity, which in the lower animals is more compressed from side to side than in the human being. Thus in the lower animals the scapula and the shoulder joint are situated almost parallel to the sagittal plane of the body, and the plane of the axis of the forward and the backward movements is definitely anterior to the origin of the long head. This change of position of the scapula and the superior extremity in their relation to the trunk gives the long head of the triceps definite power of extension, or backward movement in these lower animals. This action is further augmented by the extensive origin of the long head on the axillary border of the scapula.

In the four-footed animals where the natural position of the superior extremity is at right angles to the trunk the long head of the triceps will help in progression. In the monkey where the progression is on all the four limbs it will help in the progression as well as in climbing.

While considering the different relations of the ulnar nerve to the medial head of the triceps in man and the dog on one hand and in this monkey on the other, it is interesting to note that in both man and the dog where the ulnar nerve lies anterior (cranial) to the medial head there is a definite medial intermuscular septum, while in this monkey where the nerve lies posterior (caudal) to the medial head there is no intermuscular septum. Higher up and lower down the relations of the nerve remain unchanged in all these three animals. It seems that the change in the relation of the nerve to the medial head is only relative and is due to the different significance of the medial head in the monkey.

The absence of the medial intermuscular septum in this monkey together with the fact that the nerve lies posterior to the medial head, instead of anterior as in man and dog, suggests that the medial intermuscular septum is formed at least in part by the degeneration of some of the muscular fibres of the medial head, or from the same premuscle mass as the medial head. Originally the nerve must be passing through the premuscle mass. In those animals where the medial intermuscular septum is present, and where the nerve is between the septum and the medial head, the part of the premuscle mass lying anterior (cranial) to the nerve, instead of developing into muscle fibres forms the fibrous intermuscular septum. Though the nerve lies in such intimate contact with the medial head it does not supply the muscle in any of these animals.

The insertion of the medial head in this monkey corresponds in its position to the insertion of the subanconous of man. The medial head of the triceps in this monkey seems to be the greatly exaggerated subanconeus. In *Traité D'anatomie Humaine* by L. Testute, a case is described where the subanconous was taking extensive origin from the whole breadth of the posterior surface of the humerus.

A NOTE ON SOME ABNORMALITIES IN PLANTS COLLECTED IN BOMBAY—IV

By

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1. ABNORMAL BRANCHING IN THE ROOT OF DAUCUS CAROTA, L.

N. O. Umbelliferae

THE exposed parts of a plant such as the stems, leaves, etc., are more liable to be affected by external environmental factors than the subterranean parts, such as roots and underground stems. This is due to the fact that in the soil the conditions are practically uniform, and hence underground organs are not subject to as many changing factors as are the exposed members of plants. Moreover, the delicate primordial meristem of the root is effectively protected by the root-cap, which helps the root, in addition to its other functions, to overcome the frictional resistance of soil particles.

In *Daucus Carota*, L. the radicle grows out into a thick, fleshy, conical tap root, giving rise to fibrous lateral rootlets. In the specimen under consideration, the tap root had divided at its extremity into two branches with small fibrous rootlets as usual. One of the lateral rootlets appeared stronger than the others (Plate I, Fig. 1). The forking may have been brought about by injury to the apical growing point of the radicle, which caused the growing tip to have two apical meristems instead of one. The growing point, being composed of delicate meristematic cells may be damaged when it comes in contact with the gritty particles of the soil; particularly in this case, the root being fleshy, it is more liable to injury. Normally the root cap protects the delicate growing point, but it is quite possible that it may be injured and result in the above abnormality. Such forking is particularly common in fleshy roots as in the Beet-root, Turnip, etc.

2. DICHOTOMOUS BRANCHING IN THE LEAF OF PHYLLARTHON COMORENSE, DC.

N. O. Bignoniaceae

The normal *Phyllarthron* leaf is a unifoliate compound leaf with a jointed winged rachis, showing thereby that it has been derived from an imparipinnately compound leaf of the type found in *Crescentia alata*, *H. B & K* belonging to the same family. This is further supported by the leaf of *Citrus decumana*, *Murr.*, *N. O. Rutaceae*, in which the unifoliate compound leaf may revert to its original trifoliate nature by developing lateral leaflets, which are often seen on the plant and are regarded as instances of reversion. Similarly the lateral leaflets of *Phyllarthron* have probably disappeared in the course of evolution.

An abnormal leaf of *Phyllarthron comorensense*, *DC.* was noticed in the Victoria Gardens, Bombay. It deviated from the others on the tree in the following respects. In the middle of the first internode of the winged rachis, the axis began to fork into two, and at the node it separated into two distinct branches, each developing in the usual way into nodes and internodes with winged expansions. The lamina had dropped off from each of these daughter branches, and is therefore not seen in the figure (Plate I, Fig. 2). This is clearly an instance of forking of the same type as was described in *Gaillardia pulchella*, *Fouger.*, by the authors in a previous paper (4). It is also probably brought about by the same factors.

3. MALFORMATION IN THE LEAVES OF ARALIA GUILFOYLEI, COGN. AND MARCH, (PANAX GUILFOYLEI, COGN. AND MARCH)

N. O. Araliaceae

In many plants adventitious shoots may be developed on the stem as a result of wounding or mutilation. The tissues may be attacked at a very early period either by an insect or a fungus or virus, and due to the stimulation thus produced, an excess of nutritive material is transported to the spot, resulting in multiple, hypertrophied branching. The witches' brooms found on a large number of plants, are probably formed in this way.

In this specimen, a clear mark was seen on one of the upper branches (Plate I, Fig. 3), showing that the branch had been wounded. From below this arose a large number of new

shoots which bore etiolated and finely dissected leaves which had lacinations arising on their margins.

4. HYPERTROPHY OF THE BUD SCALES OF *MICHELIA CHAMPAKA*, LINN.

N. O. Magnoliaceae

According to Masters (8) the term hypertrophy is said "to comprise all the instances of excessive growth and increased size of organs, whether the increase be general or in one direction only". The development of parts usually suppressed, and the formation of excrescences and outgrowths can also be regarded as instances of hypertrophy.

The normal bracts which enclose the flower buds of *Michelia Champaca*, Linn. are greyish-yellow, pubescent, spathaceous, coriaceous and deciduous with a prominent mid-rib (1). In the abnormal specimen the floral bud scales were found to have outgrowths from their apices (Plate 1, Fig. 4). The mid-rib was also prolonged outwards and developed a lamina, which in

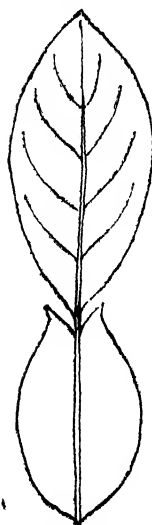


FIG. 1

certain cases, was very small and rudimentary; in others it was about $1\frac{1}{2}$ " in length and in every respect resembled the ordinary foliage leaf, except in size. Due to the continuation of the mid-rib and the other changes accompanying it, the bract seemed to be split at its apex into two distinct lobes (Text Fig. 1).

According to Goebel (5), bracts may be formed (i) by the whole leaf primordia, (ii) by the stipules, or (iii) by the leaf base or mainly so. In these abnormal specimens the bract clearly proved its stipular origin. It arose from the leaf-base and its mid-rib continued growth, thus separating the bract into two distinct lobes, representing the original stipules. The prolonged mid-rib then developed a lamina as described above.

Similar instances are reported by Masters (8) in the bracts of *Magnolia fuscata* which are sometimes found with small but perfect laminae projecting from them, and in *Magnolia Campbelli* by Hooker Thomson (6), where this phenomenon is constant.

This seems to be a clear case of reversion of the bracts to the ancestral form, *viz.*, stipules of a foliage leaf.

5. TUBULAR EXCRESCENCES FROM THE COROLLA OF
IPOMAEA PALMATA, FORSK.

N. O. Convolvulaceae

This specimen was normal in all respects except that the corolla of some of the flowers had all over the under-surface, tubular petal-like structures (Plate II, Fig. 1). Similar structures were seen by the authors in *Petunia violacea*, Lindl., N. O. Solanaceae (2); but in *Petunia* the excrescences resembled complete flowers to a greater extent, in that they possessed rudimentary stamens. The excrescences have no reference to the symmetrical plan of the flower, and may perhaps be due to the same causes which bring about hypertrophy.

The parenchyma in certain regions of the corolla is developed in excess, or the cells of that portion abnormally elongated, so as to form tubular structures known as intumescences. These are due to no parasitic influences, but result from environmental factors. One of the probable causes may be too much water in the soil. Other factors like light and temperature fluctuations may also favour intumescences. They thus represent disturbed nutrition of the cells in these regions.

6. ENATION FROM THE FRUIT OF MANGIFERA INDICA, L.

N. O. Anacardiaceae

Just near the stalk in this specimen a small fleshy outgrowth was observed (Plate II, Fig. 2). It was about $1\frac{1}{2}$ " in length and $\frac{1}{2}$ " in diameter, resembling the mango externally in colour and internally in the fleshy nature of the sarcocarp. Such a fleshy projection may be formed from the surface of the ovary during the course of its development. This abnormality is of the same nature as that seen in the extraordinary horned oranges or fingered citrons, which are commonly met with. The probable causes of this enation may be the same as those which bring about intumescences or excrescences as described above in the case of *Ipomoea palmata*, Forsk.

7. ENATION FROM THE FRUIT OF LYCOPERSICUM
ESCULENTUM, MILL

N. O. Solanaceae

As described above in the case of *Mangifera indica*, L. a similar enation was observed from the fruit of Tomato (Plate II, Fig. 3).

8. SYNCARPY IN THE FRUITS OF LYCOPERSICUM ESCULENTUM, MILL.

N. O. Solanaceae

The authors have described in a previous paper cases of fusion in *Cucumis sativus*, L., *Capsicum annum*, L., *Solanum Melongena*, L. (4). Fusion of two tomatoes (Plate II, Fig. 5) and also of three and four (Plate II, Figs. 6 and 7) are here recorded in specimens obtained from a local vegetable market. Syncarpy is common in plants with inferior ovaries. In Plate II, Fig. 5, two fruits have fused together which can also be seen clearly in the vertical section and in the increased number of the calyx lobes (Plate II, Fig. 4). In Plate II, Fig. 6, a triple tomato is shown and in Plate II, Fig. 7, a quadruple one.

9. DEVELOPMENT OF AN EXTRA CARPEL AND A SEPTUM IN THE FRUIT OF COCOS NUCIFERA, LINN.

N. O. Palmae

The normal female flower of the cocoa-nut consists of six perianth lobes in two whorls of three, and a tricarpeillary unilocular ovary, indicated by the presence of three basal pores (eyes) seen in the shell of a normal cocoa-nut. After fertilization, one of the carpels develops into a fibrous one-seeded drupe, the remaining two being abortive.

In the specimen collected, there were four pores seen on the shell instead of three. These were diagonally placed and the fruit was somewhat tetragonously obovoid, as could be clearly seen from the lines on the shell (Plate II, Fig. 8). This is probably due to the division of one of the three carpels into two. When it was cut open, it was found to deviate from the normal still further, in that there was an ingrowth in the centre, thus forming a partition, and changing the unilocular ovary into a bilocular one (Plate II, Fig. 9).

K. Cherian Jacob (7) has described a cocoa-nut having two chambers, each with its own endosperm and embryo. The specimen was normal in all other respects. The explanation given is that, two of the carpels had developed, instead of one as usual. In our specimen, the two deviations from the normal, *viz.*, the extra carpel and the internal partition are quite distinct and in our opinion, have no connection with one another. The extra carpel is due to the splitting of one of the usual three, and the partition is due to the development of two of the carpels instead of one as in the specimen of K. Cherian Jacob. In the internal view of the cocoa-nut, two of

the eyes are not seen as they occur over the dissepiment at the back. They can however be seen in the dorsal view (Plate II, Fig. 9).

SUMMARY

As in the previous three papers (2, 3, 4) the following examples of morphological abnormalities have been described and discussed :—

1. Abnormal branching in the root of *Daucus Carota*, *L.*, probably brought about by injury to the growing point.

2. Dichotomous branching in the leaf of *Phyllarthron Comorense*, *DC.* arising as a result of forking.

3. Malformation in the leaves of *Aralia Guilfoylei*, *Cogn. & March.* due to injury and local infection.

4. Hypertrophy of the bud scales of *Michelia Champaca*, *Linn.* proving the stipular origin of the same.

5. Tubular excrescences from the corolla of *Ipomaea palmata*, *Forsk.*, from the fruit of *Mangifera indica*, *L.* and from the fruit of *Lycopersicum esculentum*, *Mill.*, due to excess of food material and disturbed nutrition in the region where the abnormality occurs.

6. Syncarpy in the fruits of *Lycopersicum* due to fusion of the carpels.

7. Development of an extra carpel by the splitting of one of the three normal carpels of a cocoa-nut shown by the extra 'eye', and the development of two cells or loculi instead of one, shown by a septum, in the same specimen.

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PLATE 1



FIG. 1

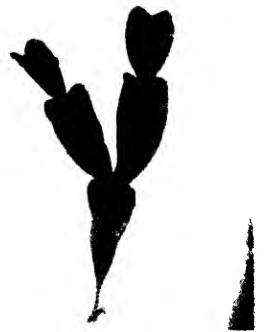


FIG. 2



FIG. III



FIG. IV

Fig. 1. Tap-root of *Daucus Carota*, *L.* showing abnormal branching. A—lateral rootlet. Fig. 2. Leaf of *Phyllarthron comorense*, *DC.* exhibiting forking, the lamina being absent. Fig. 3. Normal and hypertrophied leaves of *Aralia Guilfoylei*, *Cogn. and Mauch*: (a) Normal leaves. (b) Hypertrophied leaves. Fig. 4. Extra outgrowth on the bud-scale of *Michelia Champaca*, *L.* (a) Bud scale with outgrowth.

PLATE II



Fig. 1



Fig. 2



Fig. 3



Fig. 4



Fig. 5



Fig. 6



Fig. 7



Fig. 8

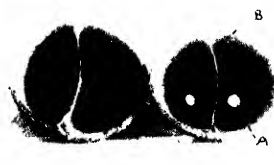


Fig. 9

Fig. 1. Excrescences on the corolla of *Ipomaea palmata*, *Forst.* (a) Excrescence. Fig. 2. An enation from a mango fruit: (a) Enation. (b) Stalk. Fig. 3. An enation from a tomato fruit. (a) Enation. Fig. 4. Fused Tomatoes: (a) Tomato with increased calyx lobes. (b) & (c) Vertical section of a double tomato. Fig. 5. Double Tomato. Fig. 6. Triple Tomato. Fig. 7. Quadruple Tomato. Fig. 8. External view of Cocoa-nut showing four eyes and four sutures on the shell. (a) Eye. (b) Suture. Fig. 9. Internal view of a Cocoa-nut showing a septum and two of the four eyes: (a) Eyes. (b) Septum.

PROLIFERATION IN THE FLOWERS OF TRICHODESMA INDICUM, *R. Br.*

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INTRODUCTION

DISEASE may cause the development of dormant or rudimentary structures, or, entirely new organs or structures, either similar to, or, entirely unlike any normal parts of the host, which may occur either on leaves, stems or flowers. In certain cases an organ may continue to produce new growths after it has reached the form or stage which would normally end its development. Thus, in many cultivated and wild flowers, the thalamus which ordinarily ceases to grow after the production of the pistil, elongates and develops either into a vegetative or a floral shoot, or sometimes the various parts of the flower become separated from one another, either by the elongation of an internode between sepals and petals, petals and stamens, stamens and pistil, or, all the three internodes become elongated in the same flower. Or, there may be the production of an adventitious bud in the axil of any part of the flower, which develops into the branch without any abnormal extension of the main axis, or, both extension of the main axis and axillary branching may be combined together. All these above mentioned cases are examples of proliferation of the normal flower, which may be due to disturbed nutrition, such as an oversupply of plastic food substances, or, fungal or animal parasitisms. This symptom, proliferation, is well illustrated in the conifers, especially in the larch (5), in which the cone axis may grow out into elongated, needle bearing branches; in the rose (5), in which a new blossom may sometimes develop from the centre of an old one; in certain composites (5) (4), in which elongated axes bearing small but perfect flower-heads may grow among the peripheral florets.

Moquin-Tandon (5) and others explain the term proliferation as the production of adventitious buds in unwanted places. The bud may be a leaf or a floral bud and it may arise from the centre of the flower, or it may develop in the axil of its bract or some of its component parts. Thus, there can be three types of proliferation, viz., median, axillary and extra-axillary, and again each may belong to either a leafy or a floral variety, according to the nature of the adventitious bud. The first two are here described.

Median Proliferation.—In this variety of proliferation, the thalamus continues its growth owing to the development of an adventitious leafy or a floral bud in the centre of the flower, and frequently this is accompanied by some other deviation in one or more parts of the flower. Examples of median leafy proliferation have been recorded in the Strawberry, *Anagalis arvensis*, *Verbascum* sp. (5), *Crotalaria striata*, DC. (3), *Sesamum indicum*, L. (4), etc. In the Strawberry the thalamus is prolonged beyond the fruit, into a small leaf-bearing branch. In *Anagalis arvensis* as described by Dr. Marchand, all the parts of the flower had assumed a green tint and were leafy in nature. In *Verbascum* sp. (5) and *Crotalaria striata*, DC., the carpels were replaced by leafy shoots. Sometimes in median proliferation, various parts of the flower become separated one from the other by the elongation of the internode (Plate III, Fig. 9). Examples of median floral proliferation are commonly met with in *Ranunculaceæ*, *Caryophyllaceæ*, *Rosaceæ*, *Primulaceæ*, *Umbelliferae* (5), etc.

Axillary Proliferation.—In axillary proliferation, one or more buds appear in the axils of any part of the flower, and according to the nature of the bud, it may be either an axillary foliar or a floral proliferation. The development of the bud or buds is not irregular but it follows some definite order. Sepals have a greater tendency than the other floral leaves to produce axillary buds, which is probably due to their more foliaceous nature. Next in frequency to the sepals, the pistil is subjected to this change, when the carpels may be either modified into leaf-like structures or disunited. The petals rank next, and lastly the stamens.

Axillary foliar proliferation of the flower is not of such common occurrence as the axillary floral one, nor is it so frequent as median proliferation. However, Masters (5) has reported about such leafy shoots from the axils of the sepals in *Brassica* sp., *Caltha palustris*, L., *Herreria¹ parviflora*, etc., and a

similar instance is here recorded by the author in *Trichodesma indicum*, *R. Br.*

Axillary floral proliferation of the flower is far more common than axillary foliar proliferation. Any part of the flower may subtend a flower bud, though probably the new buds more often originate in the axils of the sepals than in the other whorls.

CHANGES ACCOMPANYING MEDIAN AND AXILLARY PROLIFERATION

Proliferation never occurs as such. It is usually accompanied by some other changes, like alteration of form and arrangement of one or more parts of the flower. Some of these changes are briefly described below :—

(a) The calyx of a prolified flower is often modified. The sepals become foliaceous and resemble the foliage leaves in every respect.

(b) The corolla of a prolified flower also manifests a number of changes.

The petals like the sepals may become foliaceous as in a species of *Cheiranthus* (5) in which there is a constant repetition of calyx and corolla, conjoined with an entire absence of stamens and pistil.

The petals under such circumstances change their form and colour and are often modified into sepals or scale leaves.

(c) So far as the stamens of a prolified flower are concerned they may remain either unaltered, or be subjected to various changes. They may be modified into petals, scale leaves, staminodes, or, may be entirely absent.

(d) The pistil, too, is often greatly modified when affected with this malformation. It may be totally suppressed and its place taken by a foliage or a floral bud. If it is syncarpous, its constituent carpels separate from one another and make way for the prolonged axis. Very often it undergoes a still further change becoming more or less leafy in nature as in *Crotalaria* sp. (3) and in a great majority of instances, destitute of ovules.

DESCRIPTION OF NORMAL PLANT

Trichodesma indicum, *R. Br.* (2) is an annual, erect, much branched herbaceous plant, found in the rainy season in uncultivated lands. Leaves 1"–4" by $\frac{1}{4}$ "–2", variable in form, sessile

and clothed with stiff hairs. Flowers pale violet-blue, solitary and leaf opposed; pedicels $\frac{1}{2}$ "– $1\frac{1}{2}$ " long, slender and hispid; calyx deeply divided, hispid; segments lanceolate, acute, cordate at the base, and connate by the basal auricles. Corolla $\frac{1}{2}$ " long, infundibuliform, thinly hairy within. Stamens five, epipetalous; anthers conniving into a cone, hairy at the back and connective prolonged. Ovary ovoid, acute, tapering into the style and glabrous.

DESCRIPTION OF ABNORMAL PLANT

Only two abnormal specimens of *Trichodesma indicum*, *R. Br.* (Plate I, Figs. A & B) showing proliferation of the flowers were noticed during the month of August 1940 growing on waste lands in Bombay. They were periodically watched till the middle of October when they began to dry up and ultimately died. Though these two plants were growing in two different localities, they were quite identical and both of them exhibited characters in common with each other, and different from the normal ones which were growing close to them. These abnormal specimens resembled mostly the normal ones in their vegetative parts except for a few diseased shoots, which were branched more profusely than the normal ones. The leaves produced on these shoots were comparatively small, more crowded together and more prone to be yellowish, thus showing a somewhat abnormal condition. The affected branches produced flowers in the same manner as the normal branches but these flowers were greatly modified, and the degree of modification also varied with the different individuals. The flowers exhibited both median and axillary proliferations which were either foliar or floral. The different types of proliferation that were noticed are described below and are illustrated in Plates I, II, and III.

Plate II, Fig. 1, illustrates an abnormal branch bearing proliferated flowers. Both median and axillary proliferations occur here, and are occasionally accompanied by modified floral parts. The first formed flowers on the lower region of the axis were perfectly normal but the flowers that developed later, on the upper region of the axis, were greatly modified. In Plate II, Fig. 2, a branch bearing leaves is seen arising from the axil of one of the sepals, while the corolla and stamens have dropped off. On the same as well as on other affected branches, there were a few flowers in which two axillary proliferations were noticed (Plate II, Fig. 3). Here, too, the

PLATE I



FIG. A



FIG. B

Figs. A and B. Abnormal branches of *Trichodesma indicum*, *R. B.* showing proliferation.

PLATE II

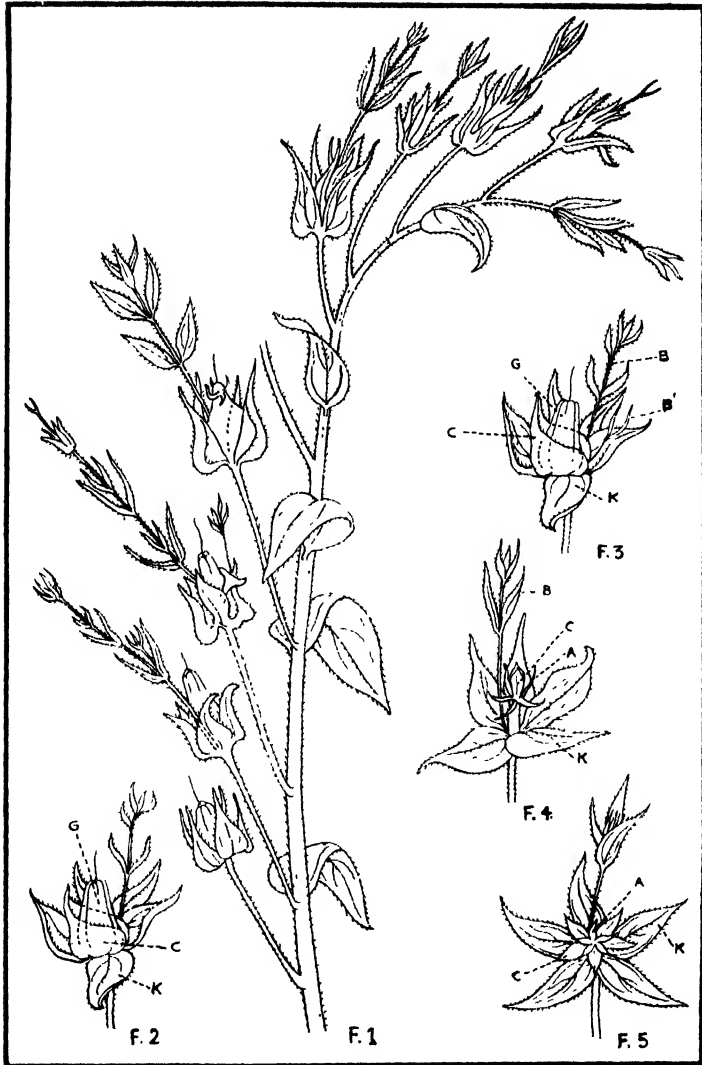


Fig 1. An abnormal branch of *Trichodesma indicum*, *R. Br.* showing axillary and median proliferations. Fig. 2. A prolified flower of *Trichodesma indicum*, *R. Br.* a branch arising from the axil of one of the sepals. B=branch ; K=calyx ; C=corolla ; G=ovary. Fig. 3. A prolified flower showing two axillary branches, each arising from the axil of a sepal. B and B'=branches. Fig. 4. A prolified flower showing axillary proliferation and modified corolla and stamens. C=corolla hypocrateriform. Fig. 5. A prolified flower showing axillary proliferation and modified corolla and stamens. C=corolla rotate.

branches arose in the axils of sepals. In Plate II, Fig. 4, the flowers not only exhibited axillary proliferation but were accompanied by some changes in the parts of the flower. The sepals had spread out and were flattened resembling the foliage leaves; the corolla had developed green colour instead of pale violet-blue, and at the same time its shape was also modified, being hypocrateriform. As for the stamens, they were much reduced in size and practically they were staminodes. The ovary in such flowers was poorly developed and the ovules were absent. In the next type (Plate II, Fig. 5), a branch had appeared in the axil of a sepal as usual, and the floral parts were correspondingly modified. The sepals had become more or less foliaceous as in the previous case, and the corolla rotate, green and of ten parts in the two whorls, five in each. The lobes of the outer whorl were almost double the size of the lobes of the inner whorl, which were linear and alternate with the outer ones. The lobes of the inner whorl were nothing but modified stamens, because various stages of transformation of stamens into petals, *viz.*, flattening of the filaments, reduction in size of the anther lobes, etc. were noticed in some of these modified flowers. The pistil was totally absent.

The median proliferation exhibited by the flowers of *Trichodesma indicum*, *R. Br.* was also very interesting. Quite a good number of flowers showing median floral and foliar proliferations was seen. Among the flowers which exhibited median proliferation, there were some, where the axis continued to grow for two or three internodes bearing opposite leaves, and ended in a floral bud (Plate III, Fig. 6); while in other instances, the axis continued its growth as a purely vegetative branch (Plate III, Fig. 7). These flowers were also modified, showing various changes in their parts. The calyx had become leafy and had spread out. The corolla had changed its shape and colour and was reduced in size. It was arranged in two whorls, the lobes of the second whorl alternating with those of the first and being comparatively small. This second whorl represented the staminodes. The pistil was absent and its place was occupied by a branch bearing foliage leaves.

In the next variety of median proliferation, the calyx was foliaceous as before, the corolla was normal and there was no trace of stamens and pistil. From the centre of this flower there arose another flower in which the calyx was absent, the corolla hypocrateriform and alternating with the corolla lobes were the metamorphosed stamens. From the centre of this second flower,

PLATE III

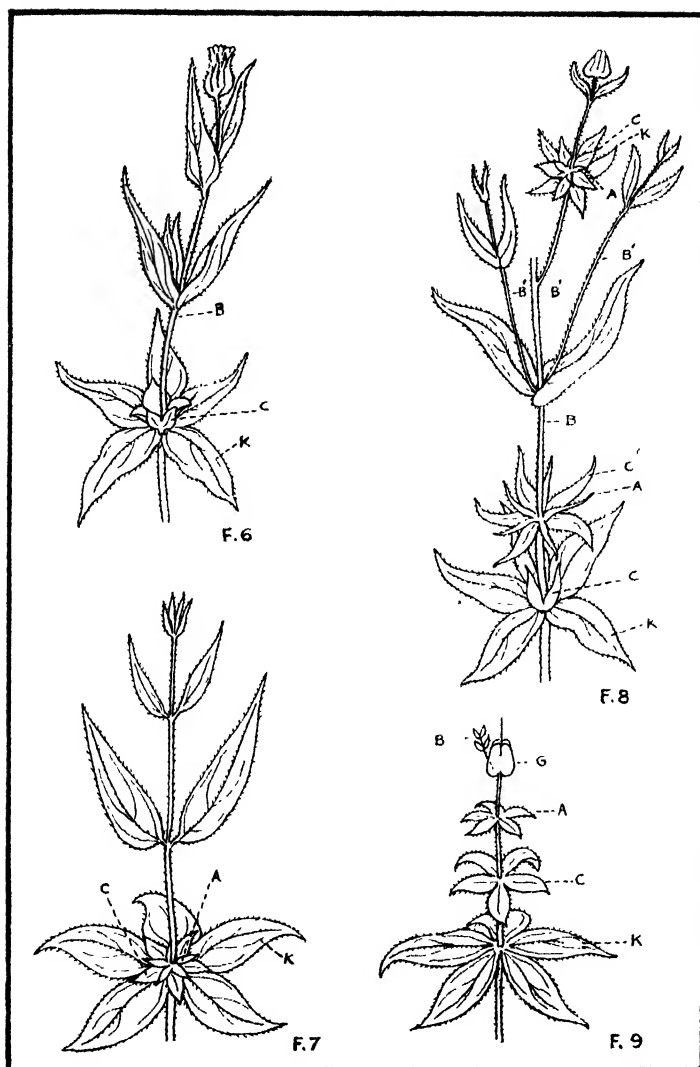


Fig. 6. A proliferated flower showing median proliferation ending in a floral bud. K = foliaceous sepals; C = modified corolla; B = branch. Fig. 7. A proliferated flower showing median leafy proliferation. K = foliaceous calyx; C = modified rotate corolla; A = staminode. Fig. 8. A proliferated flower showing median floral proliferation. K = foliaceous calyx; C = withered corolla; C' = modified hypocotyliform corolla of the second flower; A = staminode; B = branch; B' = secondary branches. Fig. 9. A proliferated flower showing apostasis. K = modified foliaceous calyx; C = modified rotate corolla on an anthophore; A = staminodes raised on a gonophore. G = pistil raised on a gynophore and showing a branch arising from one of its loculi.

a branch had developed which gave rise to a number of branches, some of which were purely vegetative and the others floral. This main floral branch, after giving rise to an abnormal flower, continued its growth giving rise to a pair of leaves and then terminated in a flower bud (Plate III, Fig. 8).

A few other flowers were seen which showed apostasis or separation of nodes and median proliferation (Plate III, Fig. 9). In these flowers the calyx was foliaceous; the corolla was hypocrateriform, green and the petals five in number. The modified stamens were petaloid, small and raised on a stalk. The ovary appeared as a normal one, except that it was raised on a gynophore, and from one of the loculi, a small branch emerged which on examination was found to be the continuation of the central axis, the thalamus. In this instance the flower has made a definite attempt to show the separation of the various floral parts by the elongation of its internodes. The structure of the flower, here, thus illustrates clearly its origin.

CONCLUSION

Proliferation may be due to one of the following causes, either singly, or, in combination with one another. Some of the possible causes are the following:—(a) unfavourable conditions of climate, (b) overnutrition or excessive food supply, (c) influence of parasitisms, fungoid or animal, (d) infection by virus, etc.

Unfavourable conditions of climate alone are certainly out of the question here, as other plants of the same species growing close by this abnormal plant did not show any sign of unhealthy condition.

The author is of the opinion that the change in floral structure and leaves is not due to a single cause but to more than one. Excessive nourishment, influence of parasitisms or attack by virus are perhaps the chief causes. Generally overnutrition leading to an excessive accumulation of plastic substances in the plant out of proportion to their utilization, may lead to great morphological changes, like phyllody, petaloidy, pistiloidy and proliferation. Such overstimulated plants are frequently more sensitive to unfavourable climatic factors and fall an easy prey to some parasitic invaders. Frog-hoppers were found harbouring on these plants, and perhaps the insects might have punctured the young tender parts of the plant and thus injected their saliva containing some viruses into

the tissue of the host, or, some parasites might have entered through the wounds, which acted as a stimulus and thus the normal balance of structure was upset which resulted in a kind of disease.

In the abnormal plant described here, two distinct changes have taken place, *viz.*, an excessive elongation of the floral axis in which the internodes have developed (Plate III, Fig. 9), and (secondly) a modification of the various floral whorls, like calyx and stamens into foliage leaves.

The author is of the same view as expressed by others that whatever be the immediate cause of this abnormality, proliferation represents a reversion to the most ancient type of reproductive axis, from which the modern angiospermous flower has been derived, *viz.*, the complex leafy shoot. This is also confirmed by the advanced knowledge obtained from the study of comparative morphology and of fossil botany.

SUMMARY

Proliferation may be either median or axillary and according to the nature of the bud, it may be either floral or leafy. Proliferation of the flower of *Trichodesma indicum*, *R. Br.* with accompanied changes in the various floral parts are described and the possible causes of the abnormality are discussed.

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VARIATIONS IN THE LEAVES OF PASSIFLORA EDULIS, SIMS.

N. O. PASSIFLORACEAE

By

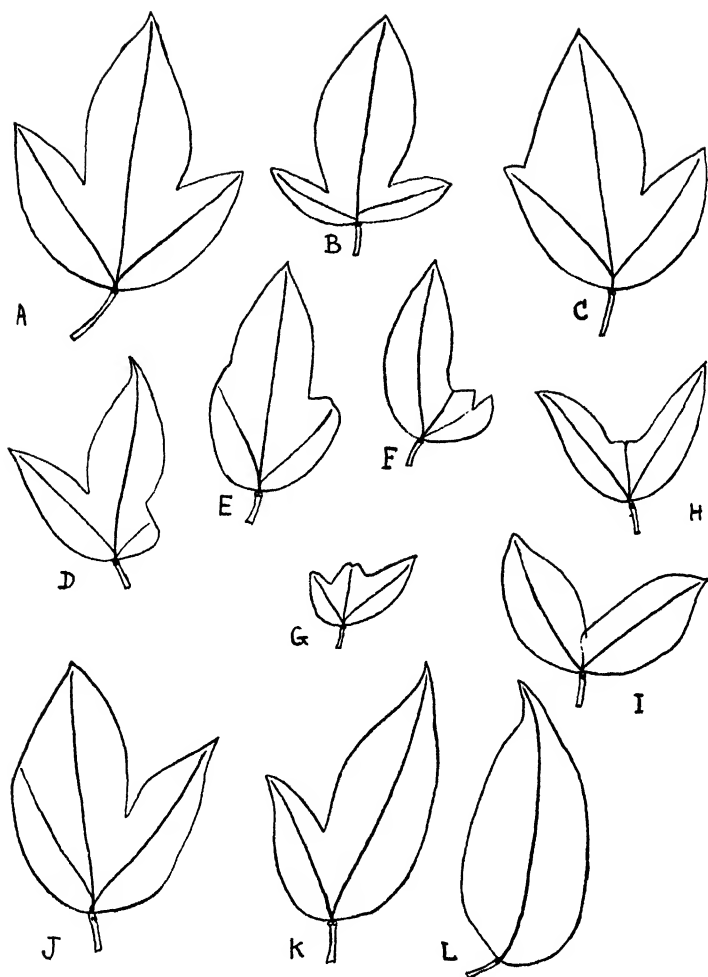
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INTRODUCTION

PASSIFLORA *edulis*, *Sims.* is an elegant climber which climbs by means of tendrils which are modification of the stem. It is a native of America and is often grown as an ornamental climber in gardens. The different forms of leaves which are described in this note were first observed and collected from the State Gardens at Junagadh in the year 1937. Later on similar types of leaves were noticed on plants growing in other gardens. It appears that it is a common phenomenon with this plant. Though such leaves are found in small number, they were mostly restricted to the apical regions of branches. They differ from the normal leaves in size and configuration. Many of them are smaller than the normal leaves.

Normally the leaves (Fig. A) are simple, stipulate, petiolate, trilobed with acute apex and serrate margin. On the upper surface of the petiole at the base of the lamina a pair of extra-floral nectaries is present. The venation is reticulately palmate with three prominent veins. Of the three veins the central one is longer than the two lateral ones. The development of the lateral veins varies. In some cases they arise from the base of the central vein which is the direct prolongation of the petiole; while in others one or both the lateral veins arise a little above the junction of the central vein and the petiole. The ptyxis of the normal leaf is plicate.



- A. Normal leaf.
- B. Hastate leaf with three prominent veins.
- C-G. Trilobed leaf with three prominent veins.
- H-J. Bilobed leaf with three prominent veins.
- K. Bilobed leaf with two prominent veins.
- L. Unlobed entire ovate leaf with one prominent vein.
(Serrate margin and smaller veins are not shown).

ABNORMAL LEAVES

Besides the normal leaves there were noticed about twelve modified forms of leaves (Figs. A-L). Some of them were found on one plant while others on other plants. The ptyxis of the abnormal leaves was plicate like that of normal leaves.

(a) There were a number of leaves, which were more or less normal but they showed a tendency to transform themselves gradually into the hastate form (Fig. B). This was due to the incision being deeper than usual. Besides, the lateral veins which were running more or less at an acute angle in the normal leaf, deviated from acute to almost right angle.

(b) There were some leaves which were trilobed with three prominent veins (Figs. C—G). In this there were five types:—

(i) In some leaves one side lobe was smaller than the other and also one of the incisions was less deep than the other; but the two side veins were more or less equal in length (Fig. C).

(ii) There were some leaves in which the incisions were more or less equal but one of the side lobe was smaller than the other and its apex was more or less obtuse or rounded and not acute. Further, in this case the side veins were unequal (Fig. D).

(iii) In the third variety there were some leaves in which the incisions were unequal like those of leaf C. One of the side lobes had a rounded apex while the other had emarginate. Besides, one of the side lobes was more reduced than the other (Fig. E).

(iv) The next type had some leaves in which the central and one of the side lobes were very much reduced. In them the veins were more or less unequal, but the position of these veins appeared to be lateral. All the three lobes had acute apices (Fig. F).

(v) The last group included leaves in which all the three lobes had undergone reduction in size. Out of these lobes the central and a side lobe were very nearly equal in size and were comparatively smaller than the other lateral lobe. Further, the lobes varied in their apices. Side lobes had acute apices while the central lobe had an emarginate apex (Fig. G).

(c) There were two kinds of bilobed leaves with three prominent veins (Figs. H—I).

In some of these leaves the central lobe was very much reduced and the two side veins were equal in length. They were longer than the mid-rib (Fig. H).

In the other kind the mid-rib was entirely reduced and the inner margins of the two lateral lobes overlapped each other (Fig. I). If the reduction were to continue still further, the leaf would be no more simple, but would become a compound binate or bifoliate leaf.

(d) There were some leaves which had two lobes with three veins. One of these was bigger than the other. There were two strong prominent veins in the bigger lobe which was the modified central. In this case either the right lobe or the left lobe was reduced (Fig. J).

(e) There were some leaves with two unequal lobes. Each of them had a prominent vein. In this case one of the side lobes was absent and the bigger lobe represented the central, the smaller the side one. In some leaves the right lobe was reduced while in the others the left lobe (Fig. K).

(f) Lastly there were some leaves in which only the central lobe was present. The lateral lobes had undergone reduction, while the developments of the lateral membranous expansions on either side of the mid-rib of the central lobe were equal in some, and unequal in others, thus producing oblique leaves in the second case (Fig. L).

DISCUSSION

Variations in leaves are recorded in the Railway creeper by Sinha (12); in *Thespesia populnea*, *Soland* by Cooper (2); in *Bryophyllum* by Majumdar (5); in *Aralia* sp. by Tewari (13); in *Euphorbia Caducifolia*, *Hains*. by Mayuranathan (6); in *Potamogeton perfoliatus* by Pearsall and Hanby (7); in *Taraxacum officinale* by Griffiths (3); and in *Hibiscus* sps. by Robinson (11).

The present case differs from Sinha (12) firstly, in that, there is the absence of an increased number of lobation and secondly, instead of two lateral lobes, all the three lobes have taken part in the modification; from Cooper (2) in that, from trilobed normal leaf simple entire (without lobe) abnormal leaf is obtained and not from entire to lobed; from Majumdar (5) firstly, in that, there is no change from simple to compound and secondly, there is the absence of periodic seasonal changes; from Tewari (13) in that, there is no change from simple to compound;

from Mayuranthan (6) in that, there is the absence of transition from lobed to unlobed condition ; from Pearsall and Hanby (7) in that, it is not aquatic but a climber ; from Griffiths (3) in that, there is the absence of periodic seasonal changes ; and from Robinson (11) in that, there is no change from unlobed to lobed.

Of these Sinha (12), Majumdar (5), Tewari (13), Mayuranathan (6) and Robinson (11) have given the descriptions only ; but Cooper (2), Pearsall and Hanby (7) and others. (3, 4, 10 and 14) have given the possible explanation as to the occurrence of those different forms of leaves.

The general outline and the character of the sub-divisions of the blade are associated with the plan of arrangement of the skeletal system of the leaf, *i.e.*, venation. The normal triple veined condition is due to the mid-rib giving off on each side near the base a strong side vein which runs up towards the summit of each lateral lobe. In the normal leaf the central lobe develops first, followed by the lateral ones.

The lateral lobes may be either equal or unequal. In some cases there is either complete suppression of one of the lateral lobes (Figs. J and K) or of both (Fig. L).

The number of lobes in the leaf is three and it is, therefore, regarded as the central or mother type. The interesting feature in the modified leaves here is, that all the three lobes take part in the modification.

The normal leaf of *Passiflora edulis*, Sims. is trilobed with both lateral lobes equal in size and configuration. In the specimens described here, all the three lobes are modified in some way or other. Even the central lobe may be modified resulting in various configurations. Sometimes it may be absent and the inner margins of the lateral lobes then reach the petiole resulting in a somewhat bifoliate compound leaf.

Usually the leaves of a species do not differ to any great extent one from another. As a general rule the leaves have their own special configuration subject to slight variation dependent upon age, condition of growth, etc. But some plants bear different kinds of leaves on the same individual. The condition is known as heterophylly.

This variation of the leaves is not the result of the action of one particular factor but of many.

According to Cooper (2) the different configurations of the leaves may be due to pathological conditions brought about

by micro-organisms which disturb the vital activity of the growing leaves.

According to Robertson (10) growth is governed by an enzyme developed within the cell at the time of cell division. This enzyme diffuses through the cell and stimulates more growth. But as the enzyme accumulates in excessive amounts, growth is checked or arrested. So these variations may be due to the checking of the growth of the lamina.

Priestly and Pearsall (9) have shown that in the case of certain plants, it is possible to change the leaf-form by changing the pressure of the water supply. When the pressure was increased, a young leaf which was normally lobulated tended to develop into a less lobulated and more entire form, while the diminution of water pressure led to the lobulation of leaves which were normally entire.

Pearsall and Hanby (8) in their study of the factors affecting the development and form of leaves showed that negative hydrostatic pressure caused leaf growth to stop or to slow down, and assumed that the rapid growth is usually associated with the presence of positive hydrostatic pressure.

Pearsall and Hanby (7) in their study concluded that variation of leaf-form in *Potamogeton perfoliatus* was the result of the chemical constituents of the medium in which the plant grew and suggested that the growth rate may be associated with the chemical and physical differences in the composition of the cell wall. These are assumed to operate by altering the rate at which nutrient materials enter the meristems. The study of the cell wall may throw light on this problem.

Besides the physiological causes, ecological factors such as light, moisture, etc. may be also responsible.

Magoesy-Dietz (4) found in *Convolvulus arvensis* four distinct types of leaves—such as auriculate or lanciolate, hastate, sagittate and elliptical—depending upon the combination of two factors—radiation and moisture.

Vaughan and Wiehe (14) are of opinion that variation in leaf area and form is due to different climatic conditions.

Worsdell (15) under the heading of simplification of foliage cites somewhat similar cases in *Cratægus Oxyacantha*, *Cratægus sinaica*, *Plantago coronopus* and *Papaver Rhœas*. In all these cases the much dissected leaves are occasionally replaced by perfectly entire ones.

These various forms of leaves are interesting from the taxonomic aspect, because the form of the leaf is of importance in the classification of species into varieties. According to Baily (1) in the majority of *Passiflora* leaves are tri-lobed. The maximum number of lobes is seven and it occurs in *Passiflora vitifolia*, *HBK.* There are some species in which the lobed condition is absent and an entire blade is present, *e.g.*, *Passiflora ligulares*, *Juso.*, *P. quadrangularis*, *Linn.*, *P. alata*, *Dry.*, *P. Decaisneana*, *Hort.*, *P. amabilis*, *Hook*, *P. laurifolia* *Linn.*, and *P. Coccinea*, *Aubl.*

The occurrence of simple entire not lobed leaves (Fig. L.) like the above stated allied species may suggest a phylogenetic relationship.

The main factor which determines the shape of the leaf here, is the rate of growth of the leaf initial. But doubtless other factors which affect the rate of growth such as the accumulation of a growth enzyme in excess, hydrostatic pressure, chemical constituents of the medium, light, moisture, climate, etc. may be responsible in bringing about variations in the leaf form.

SUMMARY

Variations in the leaves of *Passiflora edulis*, *Sims.* met with in different plants are described and it has been suggested that these may be due to not one single factor but due to several factors which affect the rate of growth of the leaf initial.

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FLORA OF MOUNT ABU

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THIS paper embodies the list of plants that were collected during my visits to Mt. Abu with our B.Sc. students on short botanical excursions. This small paper forms by no means an exhaustive treatise on the subject, and I am fully aware that the list, at present, in many ways, is very far from complete, but I hope that on some future occasion it may be possible to fill in some of the gaps.

Though great are the advantages of a general flora descriptive of all the plants of this wide tract of the country, still no one can deny the utility, in a scientific point of view, of a catalogue* of plants of a hill like Mt. Abu, of which the climate, altitude and moisture have a considerable influence on the habits and distribution of some species.

Vegetation—As the list given below is incomplete, it would be premature to offer any general remarks regarding the distribution, habits, etc., of the vegetation. As Mt. Abu is an outlier, of the Aravalli Hills in the South-East of the Indus Plain region, 5653 feet in elevation, the vegetation is more or less of the humid tropical type. With few exceptions all trees have deciduous leaves, and most of the herbaceous are dried up in the hot season.

Climate—Mt. Abu is a lofty isolated hill or cluster of hills, 7 miles to the West of the Aravalli range; the name given to the chain of rocky hills that runs South-West from Delhi through Rajputana to the northern limits of the Malva tableland. Mt. Abu is a rocky eminence rising to 5653 feet above the sea-level and crowned by the famous Dalvada Jain temple of great sanctity, a renowned place of pilgrimage for people from all parts of India as

* Miss Macdam-Plants of Mt. Abu (An old list not available).

well as for tourists from Europe and America. This hill station is the hot-weather residence of the chief officials and Rajas of Rajputana and is also resorted to by the residents of Gujarat. It is built on the hill at an elevation of 3954 feet above the sea-level. Being on the border of the arid region of western Rajputana, it shares the general characteristics as its climate, save that, owing to its elevation, it is much cooler.

The mean temperature of the year is 68°. In January, the coolest month of the year, the temperature is 58°. The lowest reading varies much in different years not having fallen below 32°. In May, which is the warmest month, the mean temperature is 79°, but the afternoon average is 89°, and the highest readings have varied from 93° to 101° in different years. The nights, however, are cool, the temperature falling, on the average, to 71° before sunrise.

The air is very dry during the greater part of the year. The mean humidity of March or April is only 29 or 30 per cent of saturation, and from November to May inclusive, in only one month it exceeds 40. In August it rises to 87. From October to May the skies are very clear. The mean rainfall of the year is a little over 63 inches. The greatest in any one year was 123 inches, and the least 19·2 inches.

Magnoliaceae :

Michelia Champaca, Linn.

Anonaceae :

Saccopetalum tomentosum,
Hook. F. & Thoms.

Berberidaceae :

Berberis asiatica, Roxb.

Fumariaceae :

Fumaria parviflora, Lam.

Cruciferae :

Nasturtium indicum, DC.
Cardamine hirsuta, Link.
Capsella Bursa-pastoris, Medik.

Capparidaceae :

Capparis grandis, Linn.
Capparis sepiaria, Linn.

Violaceae :

Viola Patrinii, DC.

Bixaceae :

Flacourtia sapida, Roxb.

Caryophyllaceae :

Polycarpon Læfflingia, Benth
& Hook.
Arenaria Serpyllifolia, Linn.

Malvaceae :

Hibiscus ficulneus, Linn.
Hibiscus tetraphyllus, Roxb.

Sterculiaceae :

Sterculia urens, Roxb.
Sterculia colorata, Roxb.
Helicteres Isora, Linn.
Melhania futteyporensis,
Munro.

Tiliaceae :

- Grewia tiliæfolia*, Vahl.
Triumfetta pilosa, Roth.

Malpighiaceae :

- Hiptage Madablota*, Gærtu.

Geraniaceae :

- Geranium ocellatum* (Cult).

Burseraceae :

- Boswellia serrata*, Roxb.

Meliaceae :

- Cedrela Toona*, Roxb.

Celastraceae :

- Celastrus paniculata*, Willd.

Rhamnaceae :

- Zizyphus rugosa*, Lamk.

Anacardiaceae :

- Odina Woodier*, Roxb.

Leguminosae—Papilionaceae :

- Crotalaria sericea*, Retz.
Melilotus indica, All.
Indigofera pulchella, Roxb.
Vicia sativa, Linn.
Pueraria tuberosa, DC.
Atylosia sericea, Benth.
Flemingia bracteata, Wight.
Dalbergia Sisoo, Roxb.
Dalbergia latifolia, Roxb.

Leguminosae—Caesalpineae :

- Caesalpinia sepiaria*, Roxb.
Wagatea spicata, Dalz.
Bauhinia purpurea, Linn.

Leguminosae—Mimoseae :

- Acacia arabica*, Willd.
Albizia Lebbek, Benth.

Rosaceae :

- Potentilla supina*, Linn.
Rosa Lyellii (wild).

Combretaceae :

- Anogeissus sericea*, Brandis.

Myrtaceae :

- Eugenia Jambolana*, Lamk.
Eucalyptus globulus (Cult).

Lythraceae :

- Woodfordia floribunda*, Salisb.

Onagraceae :

- Oenothera rosea*, Soland (Cult).

Samydaceae :

- Casearia tomentosa*, Roxb.

Ficoideae :

- Mollugo hirta*, Thunb.

Umbelliferae :

- Carum stictocarpum*, C. B. Clarke.
Peucedanum Dhana, Ham.
 Var. *Dalzelli*, C. B. C.

Rubiaceae :

- Mitragyna parvifolia*, Korth.
Hamiltonia suaveolens, Roxb.

Compositae :

- Cyathocline lyarta*, Cass.
Blumea Kingii, Clarke.
Gnaphalium luteo-album, Linn.
Gnaphalium indicum, Linn.
Artemisia vulgaris, Linn.

Campanulaceae :

- Campanula canesceus*, Wall.

Plumbaginaceae :

- Plumbago zeylanica*, Linn.
Vogelia indica, Gibs.

Primulaceae :

- Anagallis arvensis*, Linn.

Oleaceae :

- Jasminum pubescens*, Willd.

Apocynaceae :

- Carissa Carandas*, Linn.
Vallaris Heynei, Spreng. (Cult.).
Wrightia tinctoria, R. Br.
Beaumontia grandiflora, Wall,
 (Cult.).
Beaumontia Jerdoniana, Wall,
 (Cult.).

Asclepiadaceae :

- Cryptolepis Buchanani*, Roem
 & Schult.
Marsdenia volubilis, Cooke.
Asclepias curasavica, Linn,
 (Cult.).

Loganiaceae :

- Buddleia madagascariensis*,
 Lamk.

Gentianaceae :

- Limnanthemum cristatum*,
 Griesb.

Boraginaceae :

- Ehretia laevis*, Roxb.

Convolvulaceae :

- Convolvulus arvensis*, Linn.
Cuscuta reflexa, Roxb.

Solanaceae :

- Solanum nigrum*, Linn.
Solanum seaforthianum,
Physalis minima, Linn.
Datura fastuosa, Linn.
Datura fastuosa var. *alba*, C.B.C.

Scrophulariaceae :

- Celsia coromandeliana*, Vahl.
Limnophila racemosa, Benth.
Veronica Anagallis, Linn.

Bignoniaceae :

- Bignonia venusta* (Cult.)

Acanthaceae :

- Hygrophilla Serpyllum*, T.
 Anders.
Hygrophilla spinosa
 (*Asteracantha longifolia*).
Petalidium barlerioides, Nees.
Barleria Prionitis, Linn.
Barleria cristata, Linn.
Lepidagathis cuspidata, Nees.
Haplanthus verticillaris, Nees.
Adhatoda vasica, Nees.

Verbenaceae :

- Lantana indica*, Roxb.

Labiatae :

- Lavandula Burmanni*, Benth.
Pogostemon parviflorus, Benth.
Plectranthus incanus, Link.

Amarantaceae :

- Alternanthera triandra*, Lam.

Polygonaceae :

Polygonum plebegjum, R. Br.
Prodr.

Polygonum glabrum, Willd.

Rumex dentatus, Linn.

Muehlenbeckia platyclados,
Meissn.

Proteaceae :

Grevillia robusta (planted).

Loranthaceae :

Loranthus obtusatus, Wall.

Euphorbiaceae :

Euphorbia neriifolia, Linn.

Euphorbia nivulea, Han.

Phyllanthus reticulatus, Poir.

Fluggea Leucopyrus, Willd.

Mallotus philippinensis, Muell.

Urticaceae :

Holoptelea integrifolia, Planch.

Trema orientalis, Blume.

Ficus bengalensis, Linn.

Ficus retusa, Linn.

Ficus religiosa, Linn.

Ficus glomerata, Roxb.

Artocarpus integrifolia, Linn.

Salicaceae :

Salix acmophylla, Boiss.

Ceratophyllaceae :

Ceratophyllum demersum,
Linn.

Hydrocharitaceae :

Hydrilla verticillata, Gresl.

Orchidaceae :

Aerides crispum, Lindl.

Amaryllidaceae :

Furcraea gigantea, Vent.

Palmaceae :

Phoenix sylvestris, Roxb.

Lemnaceae :

Lemna polyrhiza, Linn.

Naidaceae :

Potamogeton crispus, Linn.

Cyperaceae :

Carex myosurus.

Gramineae :

Cynodon dactylon, Pers.

Dendrocalamus strictus, Nees.

Coniferae :

Pinus longifolia.

Filices :

Nephrodium cicutarium.

Cheilanthes farinosa, Kaulf.

Botrychium virginianum, Sw.

Adiantum lunulatum, Burm.

STUDIES IN BLOOMING IN THREE PUNJAB TYPES OF SESAMUM IN THE BOMBAY DECCAN

By

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SESAMUM indicum *D. C. (til)* is one of the important oil seeds of India and is grown all over India and Burma. The oil is chiefly used for culinary purposes. In the Bombay Province it is essentially a *kharif* crop although certain varieties particularly those of Gujarat are grown in the *rabi* season also. During the work on the improvement of sesamum in the Bombay Province, blooming studies in some pure types were undertaken.

The literature available on botanical work on sesamum is rather scanty. Pal¹ describes Pusa types 29 and 37 as good yielders. He states that white-seeded types are mostly early but give low yield while the black-seeded types which are late yield high. Zafar Alam and Ali Mohammad² compare three pure types of sesamum in the Punjab with respect to their maturity, oil content, yield, colour of seed coat and ability to withstand drought and disease. Kashi Ram³ gives a description of several types of sesamum grown at Pusa. He finds some correlation between rough surface of seed and low percentage of oil. Black-seeded types which have a greater branching capacity are the highest yielder while dark-brown types with smooth seed are the richest in oil content. Gammie⁴ has pointed out that of the Bombay types white-seeded ones are earlier to mature and richer in oil compared to red and black-seeded types. In Burma, Rhind and Thein⁵ have classified sesamum and described early and late types. In a cross between these two types they observe that the late character which is dominant is controlled by one principal gene. Richaria⁶ has found that the causes of low yield in sesamum are stem bending, sepaloidy and cytological irregularities. He has also

TABLE I
Morphological character of the three pure types of the Punjab sesamum

S No.	Plant Character	Type 15 (Brown)	Type 22 (Black)	Type 23 (White)	Remarks
1	From base height at which 1st branch arises on the main stem.	2.1 cms.	Mostly from base—A very few plants at 1.2 to 1.6 cms. from base	2.2 cms.	
2	Average height of plant	94.2 cms.	110.5 cms.	82.3 cms.	
3	Main fruiting branches per plant	7.2	7.6	4	Fruiting branches on main stem
4	Leaf-colour	Dark green	Deep dark-green	Dark-green	
5	Stem	Glabrous and thin	Glabrous and normal	Glabrous and thin	
6	Habit	Spreading	Spreading	Spreading	
7	Arrangement of capsules on main stem	Intermediate	Intermediate	Dense	
8	Size of capsule { Length Breadth	3.12 cms. 0.91 cms.	2.85 cms. 0.91 cms.	3.07 cms. 0.89 cms.	Average of 50 capsules
9	Colour of capsule	Dark-green	Deep dark-green	Dark-green	
10	Shape of seed	Plumpy	Less plumpy	Flat	
11	Size of seed (No. of seeds per gram)	246 (big-sized)	284 (small-sized)	278 (small-sized)	
12	Size of flower	Medium	Small	Medium	
13	Colour of corolla outside and inside	Slightly purple	Slightly purple	Slightly purple	
14	Colour of anther	Pale-yellow	Pale-yellow	Pale-yellow tinged with brown	
15	Hairiness inside corolla	Profuse and short	Sparse and long	Profuse and short	
16	General observation	Late maturing	Late maturing	Early maturing	
17	Germination percentage	96	94	94	

reported a tetraploid plant of sesamum induced by colchicine treatment⁷.

Blooming has been extensively studied in gram and also in many cereals—particularly wheat, rice, oat, barley, sorghum, *bajri* and maize. Similar studies in oil-seed crops are meagre and no reference could be found regarding sesamum. Blooming studies in sesamum were therefore undertaken on three pure types of sesamum.

MATERIAL AND METHOD

None of the collections of sesamum obtained from the Bombay Province was found to be pure. Hence three pure types 15, 22 and 26, obtained from the Oil-Seed Botanist, Punjab, were employed for the present studies. The following table gives a short description of the types as grown under Deccan conditions:—

The types were grown in four rows each 40 feet long, with 2 feet between rows and 6 inches between plants. The crop was sown on July 18th and was harvested on November 20th, 1939. Twenty plants in each type were selected for recording the date of the first flower to appear, number of flowers produced each day and in each plant, total number of days during which blooming lasted, number of capsules set, day on which the maximum number of flowers were produced, and days required for maturity.

TABLE II
Blooming in three pure types of the Punjab sesamum

S. No.	Observation	Type 15 (Brown)	Type 22 (Black)	Type 26 (White)
1	Number of days from sowing for first flower to appear ...	32	35	33
2	Total period of blooming in days ...	49	45	45
3	Total number of flowers produced in 20 plants ...	4037	4964	8746
4	Average number of flowers per plant ...	201.85	248.2	437.3
5	Number of flowers on a plant— Highest ... Lowest ...	306(4)* 101(6)	334(7) 182(3)	597(2) 209(18)
6	Number of days from sowing to maturity ..	104	100	99

* Number in brackets refers to the plant-number.

From the above table it will be seen that the three types do not differ much with respect to the number of days required for the first flower to appear from the date of sowing, the extent of period of blooming and days required for maturity. There is however considerable difference between the types in the total number of flowers produced. Type 26 (White) produces more than twice the number of flowers as compared to type 15 (Brown) and a little over one and three quarter times compared to type 22 (Black). Similarly the highest and lowest number of flowers on a plant are greater in type 26 (White) than in type 15 (Brown) or 22 (Black).

The sequence of blooming in the three types is summarised in the table below :—

TABLE III

Sequence of blooming in three pure types of the Punjab sesamum

S. No.	Observation	Type 15 (Brown)	Type 22 (Black)	Type 26 (White)
1	Percentage of blooming during the 20 days between the 16th day and the 36th day after the appearance of the first flower ...	72.2	65.0	80.0
2	Percentage of blooming during the 30 days between the 8th day and the 38th day after the appearance of the first flower ...	92.1	94.5	96.2
3	Day after the opening of the first flower on which maximum flowers opened ...	26th	22nd	24th
4	Day on which was recorded the largest rise in the number of flowers bloomed ...	22nd	7th	24th
5	Day on which was recorded the largest fall in the number of flowers bloomed ...	29th	26th	26th

The sequence of blooming shows slight variations among the types. The percentage of flowers produced in 20 days, *i.e.*, from the 16th to 36th day after the appearance of the first flower compared to the entire period shows that type 22 had the lowest percentage and type 26 the highest. The percentage compared over a period of 30 days from the 8th day of the appearance of

the first flower shows that the three types have very nearly the same percentage. A difference of a few days between the types is noticed regarding the day on which the highest number of flowers was produced.

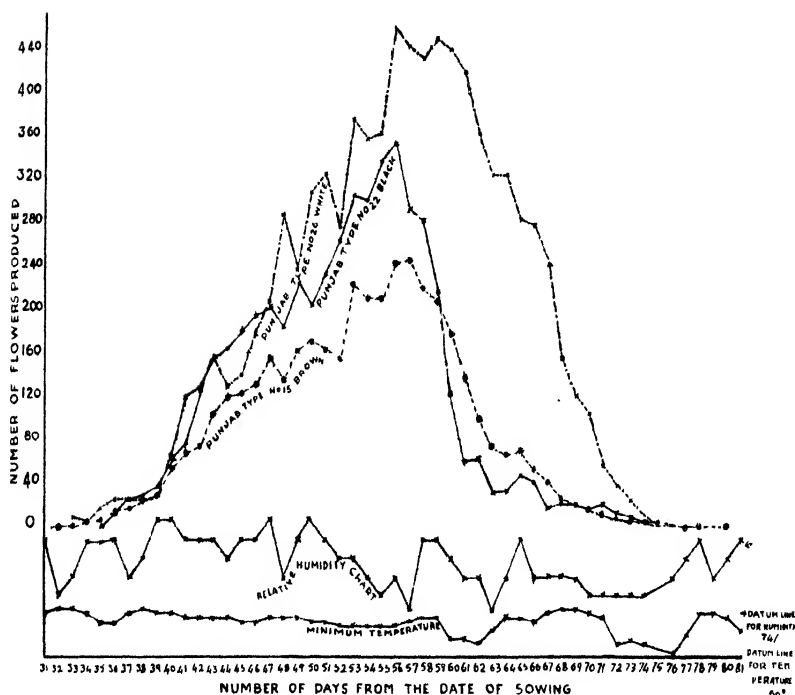


Fig. 1 : Graphical representation of sequence of blooming in the three Punjab types of sesamum.

The sequence of blooming in the three types is graphically represented in Fig. 1 which shows that on the whole, types 22 and 26 are almost alike except for minor differences as pointed out above, while the curve of type 15 is more spread out. The humidity and temperature curves given for the entire blooming period show that there is no correlation between these factors and the rise and fall in the number of flowers produced.

Capsule-setting and yield in relation to the number of flowers produced

Besides the studies in blooming described above, the relationship of the total number of flowers produced to the number

of capsules set and the yield was also determined in the 20 plants of each of the three types under study.

TABLE IV

The number of flowers produced and the number of capsules set

	No. of flowers produced	No. of capsules set	Percentage of capsules to flowers	Average Number of flowers per plant	Average number of capsules per plant	Average yield per plant in grams
Type 15 (Brown)	4037	3188	78.97	201.85	159.4	26.9
Type 22 (Black)	4964	4363	87.9	248.2	218.2	40.1
Type 26 (White)	8746	4469	51.1	437.3	223.5	30.07

From the above table it will be seen that the white-seeded type 26 which produced the highest number of flowers had the lowest percentage of capsule-setting—51.1 per cent, while the type 22 (Black) with nearly half the number of flowers gave the highest capsule-setting—88 per cent and the highest yield. Thus the number of flowers produced has no bearing either on the number of capsules set or the total yield. Yield determinations of the three types were further compared in large plant populations in the selection and the randomised trial plots.

TABLE V

Yield in grams of the three types of the Punjab sesamum

	Blooming Series		Selection Series		Yield Trial Series	
	No. of plants	Average yield per plant in grams	No. of plants	Average yield per plant in grams	No. of plants	Average Yield per plant in grams
Type 15 (Brown)	20	26.9	122	23.10	367	8.25
Type 22 (Black)	20	40.1	51	28.50	227	14.25
Type 26 (White)	20	30.07	146	17.7	247	7.7

The difference in average yield per plant in the three series in Table V is due to differences in spacing. A comparison of the three series shows that Type 26 (White) yields the lowest. Type 15 (Brown) slightly more and Type 22 (Black) the highest except in the case of yield in blooming series where Type 26 (White) yields higher than Type 15 (Brown) which difference probably is due to the small population studied.

TABLE VI

Value of 't' for comparing significance in difference between capsule-setting in the three Punjab types of sesamum

	Value of 't'		Significance of difference
	Calculated	Observed	
1. Between Type 15 (Brown) and Type 26 (White)	2.72	7.94	Highly significant at 1 per cent level
2. Between Type 22 (Black) and Type 26 (White)	2.77	9.12	Do.
3. Between Type 15 (Brown) and Type 22 (Black)	2.052	2.054	Just significant at 5 per cent level

The differences between Type 22 (Black) and Type 26 (White) and between Type 15 (Brown) and Type 26 (White) with respect to capsules produced are statistically significant at one per cent level of chance. The difference between the black- and brown-seeded types is only just significant at five per cent level of chance.

TABLE VII

Oil percentage of the Punjab sesamum grown under Deccan conditions

Year	Type 15 (Brown)	Type 22 (Black)	Type 26 (White)
1938-39	47.1	41.93	43.35
1939-40	49.25	47.4	47.35

During the first year Types 22 and 26 showed a fall in their oil content as compared to the value reported by Zafar Alam and Ali Mohammad². In the second year, however, the oil content rises probably due to acclimatisation.

DISCUSSION

The three pure Punjab types of sesamum—Types 15, 22 and 26 do not on the whole show much difference either in sequence of blooming or in many of the morphological characters except in the number of branches which is about 8 in Types 22 and 26 and about 4 in Type 15. They however show considerable differences in regard to the number of flowers produced, the capsules set and the yield. Type 26 (White) bears the highest number of flowers but sets the least number of capsules and gives the lowest yield. Not only Type 22 (Black) produces a slightly higher number of flowers than Type 15 (Brown) but it also possesses the highest percentage of capsule-setting and hence it gives the highest yield. The difference in capsule-setting between these types has been found to be statistically significant. The order of yield thus follows the order of percentage of capsule-setting. Therefore the number of flowers produced should not be taken as character for selection of high yielders in sesamum.

The yields of the three Punjab types of sesamum when grown in the Deccan are of the same order as found by Zafar Alam and Ali Mohammad² under Punjab conditions. These observations lend support to those of Kashi Ram³ and of Pal¹ on Pusa types that the black-seeded types yield more than the white-seeded ones.

SUMMARY

1. Three pure types of the Punjab sesamum, *viz.*, Types 15, 22 and 26 were grown in the Bombay Deccan and blooming and other characters were studied.
2. The character for which the types differed most was in respect of flowers produced, capsules set and yield.
3. Type 26 (White) which bears nearly twice as many flowers as the other two types had the least percentage of capsules set and consequently gave the lowest yield. Type 22 (Black) with more flowers than Type 15 (Brown) produced proportionately more capsules and gave the highest yield.
4. In the types studied, the number of capsules set bear no relation to the number of flowers produced.
5. The sequence of blooming does not appear to be affected either by temperature or by humidity.

ACKNOWLEDGMENT

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STUDIES IN THE ECOLOGY OF MANGROVES

II. PHYSICAL FACTORS OF THE MANGROVE SOIL

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INTRODUCTION

THE physical factors of the soil play a very important part in the life of the plant and especially in those of the mangroves which grow in soils which are water-logged and are very poorly aerated. Various workers like Braun-Blanquet and Pawlowski⁶, Aichinger and Siegrist⁸, and Bharucha⁴ have emphasized this point of view and shown that certain plant associations depend on the physical conditions of the soil. Not only is the study of the physical composition of the soil important from this point of view but also from that of the

classification of soils ; and this is especially true of the mangrove soil since it remains so far practically uninvestigated, as reference to recent standard books on pedology will show.

•"

(A) PHYSICAL ANALYSIS

As the chemical composition of the soil is partly dependent upon its physical structure, an attempt was made to study the air- and water-content, the air- and water-capacity and the proportion of the solid particles of the soil of *Avicennia alba* Association.

For the determination of the above factors, Ramann and Burger's method, modified by Siegrist¹⁰, was followed. The details and actual working of this simplified method were described by Bharucha⁵ in a paper, read before the Botany Section of the 21st Indian Science Congress held in 1934 at Bombay.

Apparatus.—It consists of—(1) a hollow iron cylinder of 250 c. c. capacity, open at both ends ; one of its edges is sharpened to facilitate its working ; (2) two lids to cover the cylinder ; (3) two lids with perforations to cover the cylinder when the latter is placed in water ; (4) two round pieces of white cloth of the same size as the lids ; (5) a glass jar of about 6" dia. with a tin cover fitted with a valve ; (6) a suction pump ; and (7) an aluminium box of 70–80 c. c. capacity (Fig. 1).

Method of working.—At first the ground from which the sample of soil is to be taken is scraped off of its vegetation. The iron cylinder is then forced into the soil as gently as possible, so that the physical structure of the soil is least disturbed. This is best done by rotating gently the cylinder when it is forced into the soil. The cylinder is let into the soil till its upper edge is in level with its surface. After this operation is over, the soil round the cylinder is dug up gently and the cylinder is lifted out. Any soil that may be protruding out of the cylinder is cut away gently with a sharp knife. The cylinder is then closed with two non-perforated lids and brought to the laboratory.

A separate sample of the same soil (about 50 grms.) is brought at the same time as the cylinder, in an air-tight aluminum box to determine the water-content of the soil.

The cylinder on being brought to the laboratory is cleaned from outside and the lids taken away. In place of the latter two pieces of white cloth are put and the cylinder closed at each

end with the perforated lids. The latter are kept in position by an elastic band. The cylinder thus prepared for experiment is weighed without the elastic band. After weighing it is placed in the glass jar full of water for two to three hours.

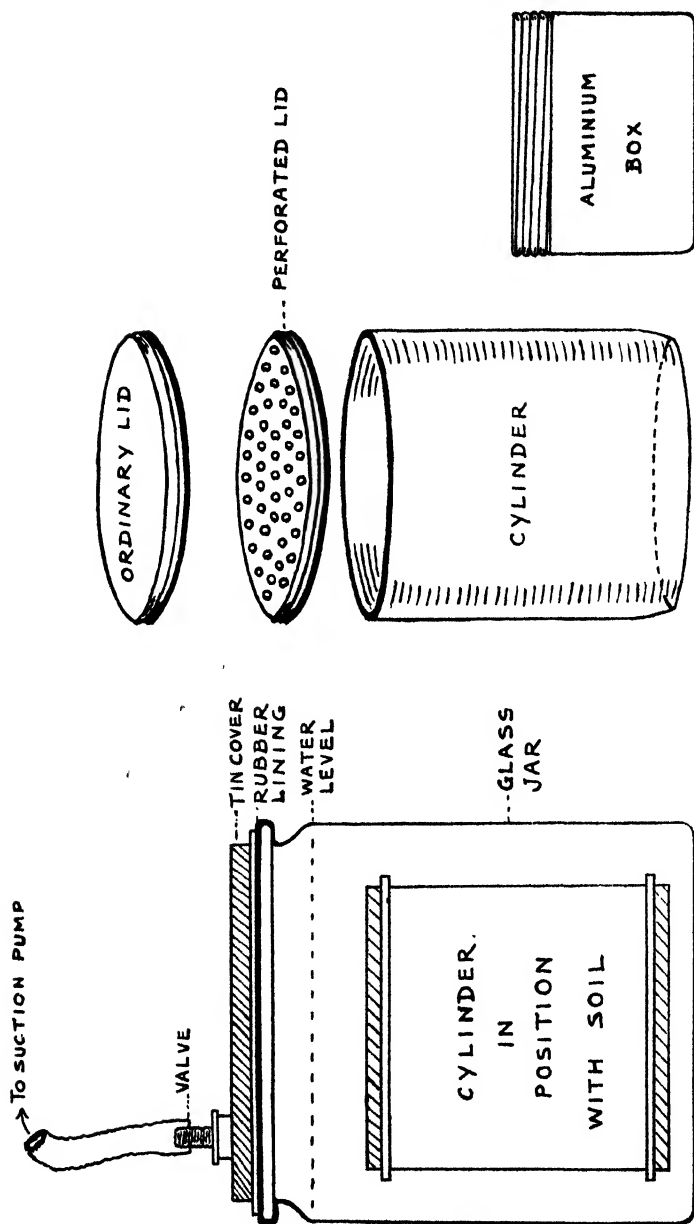


Fig. 1—Apparatus for finding out the Physical Factors of the Soil.

At the end of that period most of the air in the soil sample will be eliminated. To make sure that all the air is driven off from the soil sample, the valve of the lid of the glass jar is connected to a suction pump. The pump is worked gently to prevent soil particles from being sucked, till no air bubbles come off from the soil sample. The cylinder is then taken out from the glass jar, dried quickly with a piece of cloth and reweighed immediately after, without the elastic band. The difference in the first and second weights gives the "air-content" of the soil or gives the weight of the water required to fill in the air-spaces. The final result is expressed as percentage of the volume of the fresh sample of soil.

After weighing the cylinder for the second time, it is placed on a sieve for about two hours to allow the water from the soil sample to drain off. The cylinder is then reweighed. The difference between the second and third weights gives the "air-capacity" of the soil. The result is expressed as percentage of the volume of the fresh weight.

The "water-content" of the soil is determined by drying the other sample of the soil that was brought in the aluminum box. The result is then calculated on the amount of soil contained in the iron cylinder and expressed in percentage of the volume.

Knowing by now the "water-content" and the "air-content" of the fresh sample of the soil, the weight of the "solid particles" is obtained by subtraction from 100 the total percentage weights of water and air of the soil.

The "water-capacity" of the soil is deduced by subtracting the percentage weights of the "solid particles" and the "air-capacity" from 100.

Thus :

Fresh soil = Air-content + Water-content + Solid particles.

Saturated soil = Air-capacity + Solid particles + Water-capacity.

Thus four physical factors of the soil are obtained simultaneously by the use of the above simple apparatus.

Definitions.—By *Water-capacity* is meant the "Water-content" of a "saturated" soil allowed to drain for two hours or so; or according to Ramann, "Water-capacity" is the faculty of

a soil to absorb or retain water in a liquid state for a reasonable time or for a period sufficiently long.

By "*Air-capacity*" is meant the quantity of air contained in "saturated" soil which is allowed to drain for about two hours.

Results

TABLE 1

Monthly readings for the Colaba soil of *Avicennia*
alba vegetation

Date	Percentage volume on fresh weight					Season
	Air-content	Water-content	Air-capacity	Water-capacity	Percentage of solid particles	
27-2-37	1.38	62.03	2.77	60.64	36.59	Hot
22-3-37	6.44	50.83	4.16	53.11	42.73	
22-4-37	3.76	54.49	2.90	55.36	41.75	
18-5-37	3.80	48.54	2.39	49.95	47.66	
18-6-37	3.73	53.13	4.97	51.89	43.14	Rainy
15-7-37	3.71	45.70	2.91	46.50	50.59	
23-8-37	2.61	58.17	3.47	57.31	39.22	
23-9-37	0.28	48.96	4.03	45.21	50.76	
7-10-37	1.66	50.44	1.38	50.72	47.90	Cold
19-11-37	0.57	51.87	2.00	50.44	47.56	
8-12-37	2.88	50.25	1.57	51.56	46.87	
10-1-41	1.66	70.30	3.95	68.01	28.04	
Yearly average	2.71	53.72	3.04	53.39	43.57	

(a) *Water—and Air-contents.*—It is well known that the greater the amount of water in a soil, less is its air-content; that is to say these two factors vary inversely. This is borne out by Table 1—Fig. 2, in which the fluctuations in the water- and air-content during one full year are represented graphically. It will be further seen from it that the water-content is very high throughout the year, varying from 70 per cent in January to 45.7 per cent in July and that it fluctuates throughout the year. On the contrary, reference to the same figure will show that the air-content of the soil is very poor and does not fluctuate much. Its variation is from 0.28 per cent in September to 6.44 per cent in March. Thus it will be seen from both the graphs that there is an influence on the water- and air-contents of the soil of the seasons, but it is much more marked in the former than in the latter.

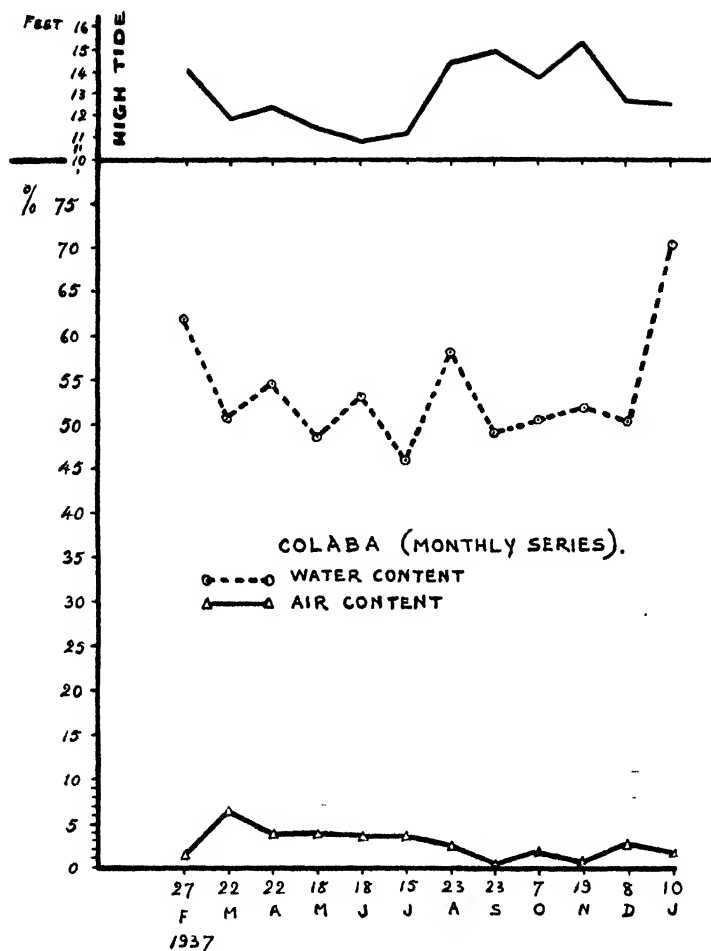


Fig. 2

Further it will be seen from the same figure that the water-content curve is directly proportional to the high tide curve in the hot and cold seasons, while in the months of monsoon a slight irregularity occurs. This result seems to be reasonable, as when the soil is flooded with water during the high tide, the water-content is expected to rise. But in the monsoon this regularity is not seen according to the tide as the soil may have an additional water from the showers and drainage at odd times in this season and as such the tidal effect is not marked.

The above monthly results of the water-content calculated on the fresh weight of the soil are confirmed by the weekly

results which are given in Table 2 and represented graphically in Fig. 3.

TABLE 2

Weekly percentage readings of water-content of the Colaba soil of *Avicennia alba* vegetation on fresh weight basis

Date	Percentage of water-content on fresh weight basis
5-8-39	59.17
12-8-39	66.29
19-8-39	65.44
2-9-39	69.47
9-9-39	58.17
15-9-39	66.71
23-9-39	63.96
30-9-39	61.34
6-10-39	62.92
13-10-39	62.72
20-10-39	64.92
26-10-39	55.42
2-11-39	63.42
8-11-39	58.46
17-11-39	62.66
23-11-39	68.21
30-11-39	64.28
7-12-39	62.43
14-12-39	67.73
21-12-39	64.34
28-12-39	68.72
4-1-40	64.17
11-1-40	68.87
18-1-40	68.88
22-1-40	65.46
22-1-40	68.72
25-1-40	66.20
1-2-40	69.78
8-2-40	69.19
15-2-40	68.80
22-2-40	69.17
29-2-40	69.74

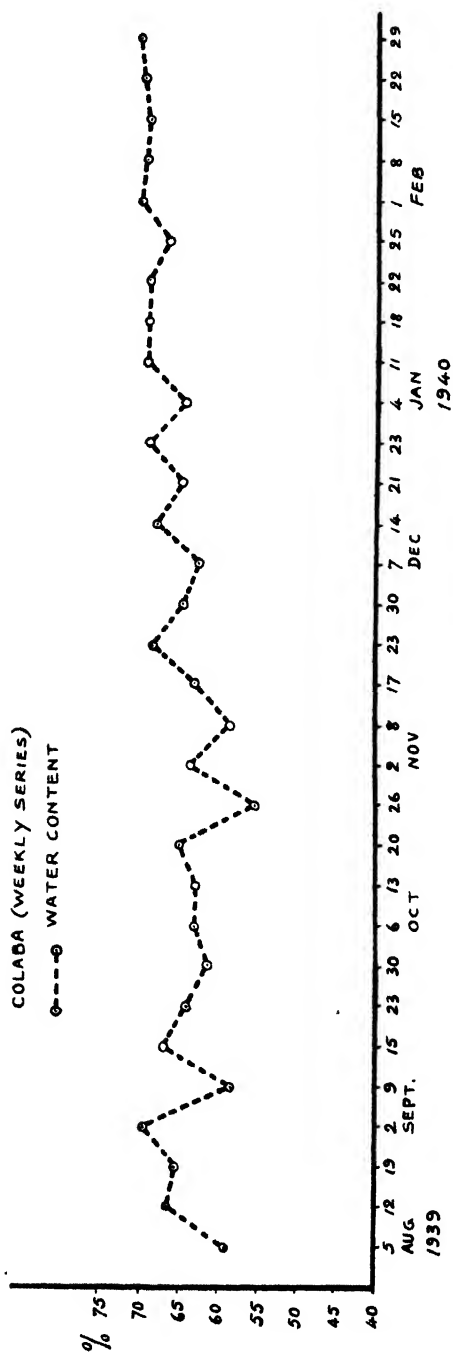


Fig. 3

(b) *Water-capacity and Solid particles.*—Bharucha⁴ has shown in his work that the water-capacity of the soil diminishes with humidity and increases with dryness. This conclusion is confirmed by the present results which are given in Table 1 and shown in Fig. 4. For example in the monsoon the water-capacity is appreciably diminished. On the other hand during winter and summer it has increased. The explanation for this phenomenon was offered by Bharucha (*ibid*) by saying that during a dry period the soil contracts and breaks due to the loss of water. As a result the fine particles of soils are increased and thus expose a greater surface for adsorption. Hence the number of fine particles in a unit volume (that is to say in the same size cylinder) is greater

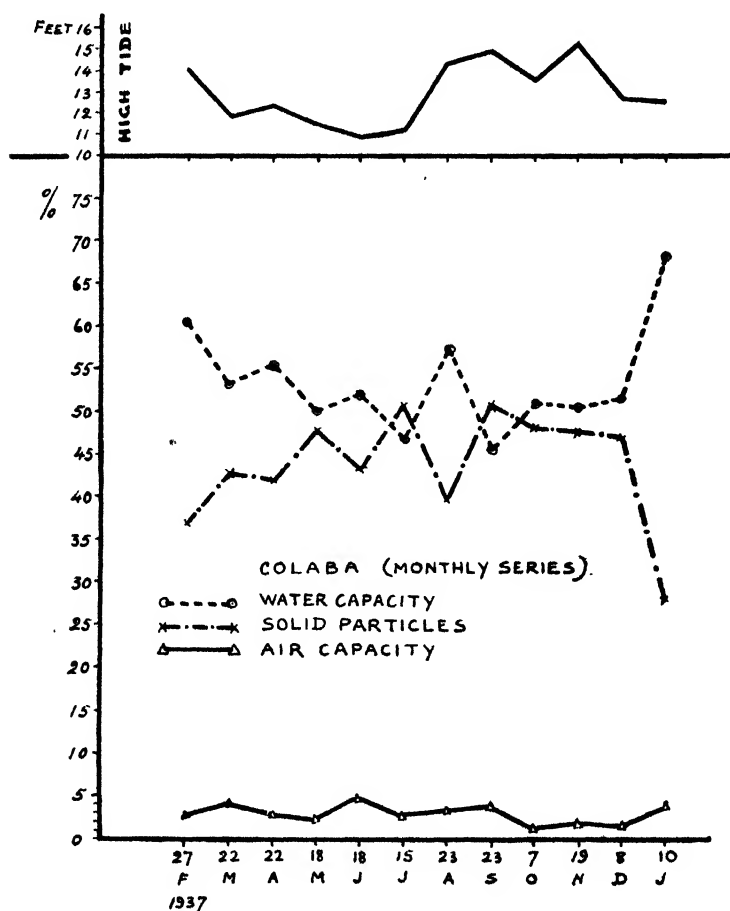


Fig. 4

in summer than during the rainy period when the cracks in the soil disappear and the soil dilates. Thus the water-capacity of the soil increases during the dry period on account of the greater number of fine particles which retain greater amount of water.

During a moist period the aggregation of fine particles takes place thus exposing lesser surface area for adsorption. That is why water-capacity, that is to say the power of retention, diminishes. Thus it will be seen from Fig. 3 that the curve for water-capacity and for solid particles run inversely.

(c) *Air-capacity*.—Braun-Blanquet and Pawlowski,⁶ Aichinger and Siegrist⁸ have shown that the air-capacity of the soil increases simultaneously but not proportionately with water capacity. Bharucha¹⁰,⁴ working on a dry type of soil has confirmed these results. But the present investigations which are on a soil totally different from the above ones do not confirm these results. This is probably due to a very little variation that is found in the air-capacity of this soil throughout the year. (Table 1—Fig. 4).

The same workers interpreted their results in terms of the effect of rainfall on the soil. Here it is evident from the results that the rainfall has not so much effect on the air-capacity or the water-capacity of the soil since these soils are constantly influenced by another very important factor namely by the tidal waters which keep the soil constantly moist.

(d) *Water-content of other soils*.—Finally attention may be drawn to occasional determinations of the water-content of two other types of soils namely under *Sesuvium portulacastrum* and *Suaeda fruticosa*.

TABLE 3
Occasional readings of percentage water-content of the
soil from Vadala vegetation

Date	<i>Sesuvium portulacastrum</i> Fresh weight	<i>Suaeda fruticosa</i> Fresh weight
7-2-37	53.52	—
13-3-37	45.38	—
4-6-37	36.09	42.07
17-6-37	43.82	32.95
12-8-37	50.54	49.67
2-9-37	47.84	48.56
23-10-37	48.80	43.83
23-11-37	44.92	46.70
21-12-37	45.73	45.20

In Table 3 are given occasional readings of the percentage of water-content of the soil under cover of *Sesuvium portulacastrum* and *Suaeda fruticosa*. The results which are represented in Fig. 5 show that the soil under the former is moister than under the latter.

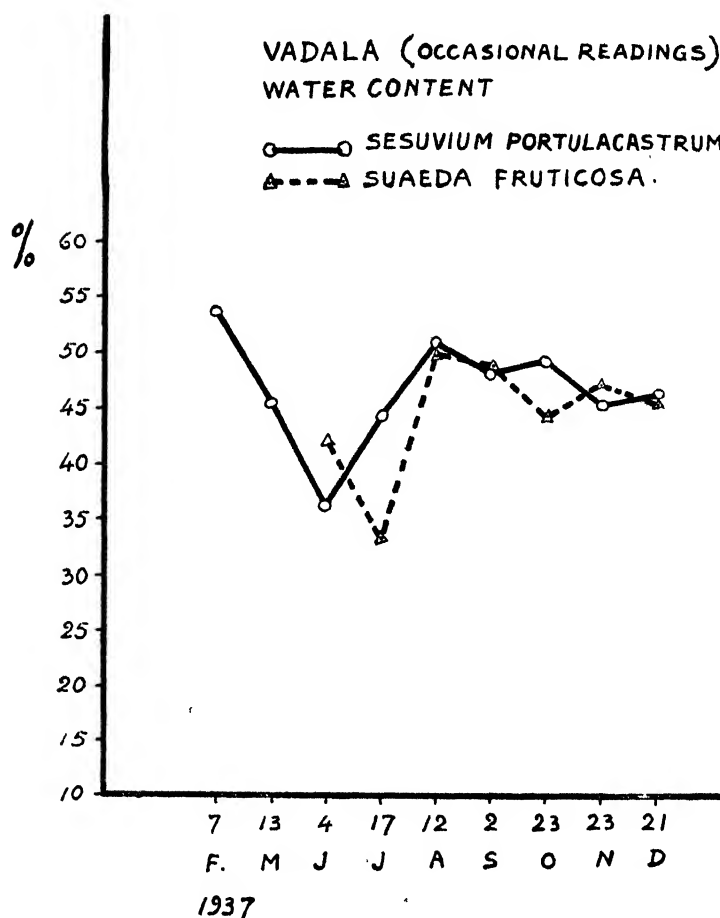


Fig. 5

(B). MECHANICAL ANALYSIS

On arrival at the laboratory the soil is spread out to dry at room temperature and then a weighed sample is prepared by passing it through a 2 mm. round hole sieve, taking care to break off previously any lumps and gently disintegrating it in a mortar with a wooden pestle. The residue left on the sieve is weighed and expressed as a percentage of the total weight of the air-dry soil sample. The material passing

through the sieve is the bulk sample from which separate sub-samples are carefully and uniformly taken for grading into following fractions : —

TABLE 4

The diameters and settling depths and times of the fractions according to the international scale

	Depth	Time	Corresponding diameter
Clay	10 cms.	8 Hrs	0.002 mm.
Silt	10 cms.	4 mins. 48 secs.	0.02 mm.
Fine sand	Separated by 0.2 mm. sieve		0.2 mm.
Coarse sand			2.0 mm.

Method.—The grading into fractions consists of two distinct operations, *viz.*, (i) dispersion, and (ii) the actual mechanical analysis.

The actual mechanical analysis of the dispersed sample was carried out according to the Revised Official Method^{1 & 2} for the mechanical analysis of the soils by using the special pipette method. The dispersion was carried out according to Chakraborty's method^{7 & 8} in which the organic matter is first oxidised, using alkaline permanganate for oxidation.

After oxidation of the organic matter, the soil suspension is made upto one litre in a measuring cylinder after adding Na OH to bring the pH to 10.5 and shaking for 6-8 hours in a shaker having a speed of 40 revolutions per minute. Then the contents of the cylinder are thoroughly shaken by hand by repeated inversions of the cylinder for one minute, seeing that any sediment which settles at the bottom is thoroughly mixed up with the liquid. The cylinder is then allowed to stand and the first sampling is made at 10 cm. depth when the well shaken suspension has stood for 4 minutes 48 seconds. The pipette with the top closed, is lowered vertically into the suspension to the required depth (this operation is begun about twenty seconds before the time is up) and 20 c.c. of the suspension is withdrawn with care to avoid too rapid ingress of the liquid, which might cause eddying in the bulk suspension.

The contents of the pipette are rapidly adjusted to the mark and delivered in a tared dish. The contents of the dish are then dried at 105° C. on a water-bath, cooled in a desiccator, weighed and represented as percentage of clay and silt. The actual calculation is reduced to dividing the number of milligrams of

the oven-dry material by four (since the original concentration of the suspension in the cylinder was 2 per cent).

The contents of the cylinder are again shaken up for one minute and are allowed to settle for eight hours and afterwards sampled at a depth of 10 cm. below the new surface level, from which the percentage of clay is obtained, after drying, cooling and weighing as in the previous case. Thus the two operations give silt plus clay, and clay, and from these the percentage of silt is obtained by subtraction.

Coarse sand and fine sand are estimated directly. After the clay sampling the bulk of the supernatant liquid is poured away and the sediment in the cylinder is transferred to a 400 c.c. beaker and made up with water to a height of 10 cm. above the base. It is then well stirred up and allowed to settle for 4 minutes 48 seconds, and then the turbid suspension is poured away. The beaker is again filled to the mark with water and the process is repeated until the liquid is no longer turbid at the end of the period. The residue is a fine sand, which is collected, dried and weighed as above.

Table 5 gives the statement of results on the air-dry soil.

Results

TABLE 5

Results of the analysis on air-dry soil of *Avicennia* vegetation from Colaba

Date	27-2-37	8-12-37
Coarse sand	4.00	3.90
Fine sand	38.15	38.57
Silt	33.07	29.50
Clay	3.85	4.25
Moisture on air dry soil	3.44	5.38
Calcium carbonate	4.58	7.82
Loss on ignition	11.59	10.29
Difference (errors of experiment)	1.32	0.29
Total ...	100	100

From the above Table it is clear that the percentage of fine sand is the highest of all the soil constituents. The mean comes

to 38.36 per cent. The next figure is of silt which varies from 29.50 per cent to 33.07 per cent. The coarse sand and clay vary from 3 to 5 per cent. Besides these the carbonates, the moisture-content and the loss on ignition were determined, and all were added together. The difference after deduction of the above total from 100 was expressed as the difference due to experimental error.

CONCLUSIONS

Since the proportion of fine sand and silt varies from 68 per cent to 71.3 per cent, the soil may be said to be made of finer particles and may be classified as sandy and silty.

The above analysis reveals for the first time the true nature of the mangrove soil and shows that in addition to high salt-content the mechanical structure of the soil is another important unfavourable factor which hampers the plants from absorbing water readily from the soil. Also it shows why the mangrove soil is poorly aerated (*cf.* p. 8).

Thus these investigations further strengthen Schimper's theory⁹ of the "physiological dryness" of the mangrove soil and explain in part the high osmotic pressure of the mangroves.

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THE BIOLOGICAL SPECTRUM OF THE MADRAS FLORA

By

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AND

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INTRODUCTION

IN a previous paper¹ we have stated that except for one small paper by Borgesen², no study was so far made in India on the basis of Raunkiaer's Life-Form system. To support or disprove his main conclusions it was necessary to choose several places in India differing in their geographical, climatic and floristic features. But to do this it was also necessary that for places chosen there should be available all the data for the proper interpretation of the results. These are unfortunately not available for many places in India due to want of (1) climatic data or (2) lack of regional floras or both.

However, we could find a few places in Southern India and Madras is one of them. Mayuranathan's³ "Flora of the Madras City and its Environs" is very exhaustive, containing as it does description of as many as 689 species. Also the study of the biological spectrum of Madras would form a contrast to our former study of Matheran and Mahabaleshwar¹ as it lies on the East coast of India and as such comes under the influence of the north-east monsoon.

The present work on the life-forms of the plants is based not merely upon the above-mentioned flora³ but also upon Gamble's Flora of the Presidency of Madras⁴ and Hooker's Flora of British India⁵.

1. PHYSICAL FEATURES

Topography.—Madras, the capital of the Madras Presidency, is situated in 13°4'N latitude and 80°17'E longitude, on a

plain only 40 ft. above sea level. It covers an area of 30 sq. miles, extending about 9 miles in length along the coast and 2 miles in breadth.

For centuries before the advent of the English and the building of Fort St. George in 1639, Madras was a group of scattered villages.

The eastern portion of the City consists of a dune running along the coast, while the western portion is made up of a parallel trough, crossed by the Cochrane's Canal, formerly known as the North River. The Buckingham Canal runs through the entire length of the City and traverses the Cooum River which divides it into two parts.

Fort St. George is the centre from which the City has extended north, south and west. On the north-east, the Royapuram Beach and Tondiarpet form the boundary, while San Thome Cathedral forms the south-eastern boundary. The north-western area consists of the Buckingham and Carnatic Mills.

The City has recently extended its limits by including Mambalan or Theagarajanagar on the south-western border of the City⁷.

Climate.—Madras, lying as it does at $13^{\circ}4'N$ latitude and $80^{\circ}17'E$ longitude, has a climate characteristic of the north tropical zone which is influenced by the north-east trade winds.

It is not influenced by the south-west monsoon as it brings rain in May on the Malabar coast but during its passage through the Peninsula, the monsoon current loses most of its moisture leaving practically little or no rain for the east. From June to September, a low pressure area is produced north of Madras which brings westerly and south-westerly winds. In the City the winds are strongest in June. The low pressure area then moves southwards changing the direction of the wind from the south-westerly to the north-easterly. The north-east monsoon brings rain to the City in October and November. Thus Madras City receives rain during the retreating south-west monsoon period, when there is a conflict between the waning south-westerly current and the advancing north-east monsoon wind. The north-easterly winds blow till the end of February, the velocity gradually diminishing. In March and April the direction changes from easterly to south-easterly or southerly.

The hot and dry season of Madras begins from the middle of December and ends in the middle of June. During this

period of six months the rainfall amounts to only 6 inches, half of which is brought by storms.

The wind changes its direction from north, north-east in December through east to south-west in June, resulting in climatic changes. In February the direction is eastwards. From March to June, the wind increases its strength and in the month of April and May, the general direction changes to southerly shore winds^{7, 9}.

The records of the monthly and annual rainfall are given below in Table 1 and the corresponding graph showing the maximum amount of rain is given in Fig. 1 :—

TABLE 1

Rain- fall in	J.	F.	M.	A.	M.	J.	J.	A.	S.	O.	N.	D.	Annual
Ins.	0.79	0.31	0.20	0.48	1.78	2.61	4.12	4.81	4.34	10.80	13.60	5.75	49.68
Cms.	2.0	0.78	0.73	1.21	4.52	6.62	10.46	12.21	10.92	27.43	34.52	14.60	126.18

The rainfall in the dry season is scanty. Occasional showers known as Pongal Showers take place in January due to the revival of the north-east monsoon conditions in the south of the Bay. Fewer showers occur in the months of February and March.

The records of the maximum, minimum and mean monthly and annual temperatures are given in Table 2 :—

TABLE 2

Temp.	J.	F.	M.	A.	M.	J.	J.	A.	S.	O.	N.	D.	Annual
Max in °F	85.2	87.1	89.5	92.4	97.9	98.3	95.3	93.7	92.7	89.6	85.7	83.9	90.9
Min. in °F	67.3	68.0	71.7	77.1	80.9	80.6	78.5	77.2	76.6	74.6	71.9	69.3	74.5
Mean in °F	76.25	77.55	80.6	84.75	89.40	89.45	86.9	85.45	84.65	82.10	78.8	76.60	82.7
Mean in °C	24.58	25.30	27.0	29.30	31.88	31.91	30.5	29.68	29.25	27.82	26.0	24.77	28.1

From January to June the temperature gradually rises and from July to December it gradually falls. The maximum temperature is recorded in June.

The records of the monthly and annual humidity (Table 3) clearly show that the atmosphere must be dry as the annual humidity amounts to only 72 per cent. the lowest occurring in the month of June when the temperature is maximum. The humidity reaches its maximum of 79 per cent. in November when the rainfall is heavy, and its minimum of 62 per cent. in June. From July onwards, the percentage increases, and the moist atmosphere together with the high temperature produces great discomfort :—

TABLE 3

J.	F.	M.	A.	M.	J.	J.	A.	S.	O.	N.	D.	Annual
73%	73%	73%	73%	67%	62%	65%	70%	72%	78%	79%	77%	72%

Madras enjoys a long period of sunshine having on an average 2400 hrs. of bright sunshine in a year out of a total of 4400. This affects the vegetation considerably and its effect is accentuated by the high winds⁷.

Cyclones and storms visit Madras nearly every year, resulting in great damage to life and property. Except February, storms occur every month of the year, being strongest in the months of May and June or October and November. The pre-monsoon storms differ from those of the latter months in the direction of movement. At times they cause severe winds and heavy rainfall on the coast. The post-monsoon storms bring rain during October and November.

2. HYDROTHERM FIGURE*

In Tables 1, 2 and 3 are given the figures for rainfall, temperature and humidity for Madras and they are represented

* The hydrotherm figure for any region according to Raunkiaer is a figure showing the relationship between the temperature curve, plotted in degrees Centigrade and the precipitation (rain) curve, plotted in Centimetres, in the same graph.

in Figures 1 and 2. From both of them, it will be seen that

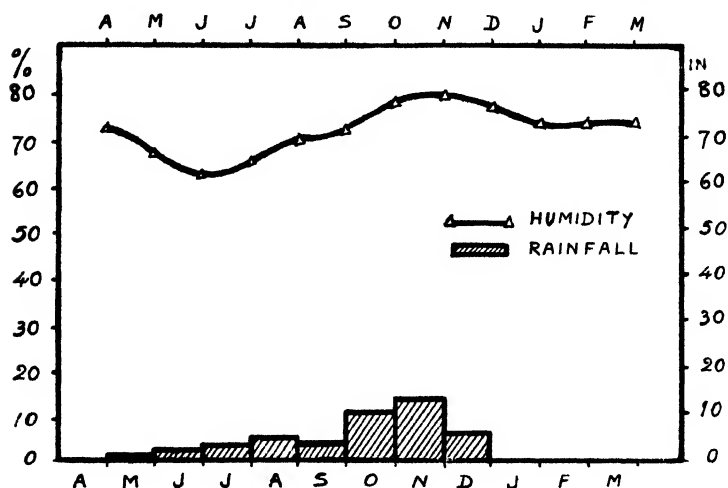


Fig. 1

HYDROTHERM FIGURE

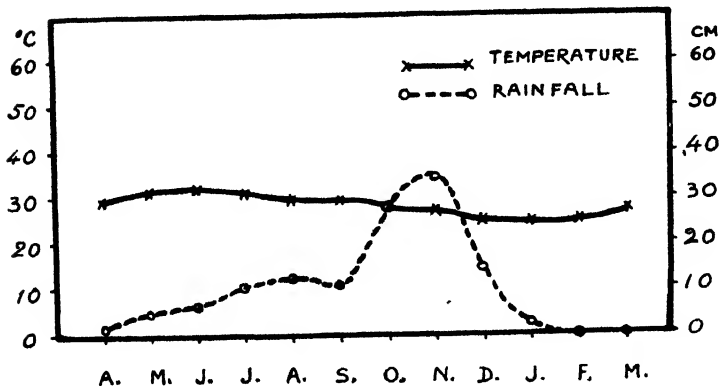


Fig. 2

the temperature is high and constant, which is indicated by the straight curve. On the other hand, the rainfall ranges from a little above zero to about 35 cm. in the month of November, when the curve reaches its maximum height, after which it falls and finally sinks to below 5 cm. from January to May. From May the curve rises till November, its upward course only interrupted by a slight dip or depression in

September. The dry or the unfavourable season therefore extends from the beginning of January to the end of May.

3. THE BIOLOGICAL SPECTRUM

TABLE 4

Names of Places	No. of Sps.	The percentage distribution of the species among the Life-Forms				
		*Ph.	Ch.	H.	Cr.	Th.
Madras ...	689	34	23·5	9·7	5·1	17·9
Aden ...	176	34	27·0	19·0	3·0	17·0
Timbuctoo ...	137	24	36·0	8·0	6·0	26·0
The Libyan Desert...	194	12	21·0	20·0	5·0	42·0
Cyrenaica ...	375	9	14·0	19·0	8·0	50·0
Normal Spectrum ...	400	46	9·0	26·0	6·0	13·0

In the above Table are given the biological spectra for Madras, Aden, Timbuctoo, the Libyan Desert and Cyrenaica together with the Normal Spectrum. From it, it will be seen that the Life-Form which exceeds most in the percentage number of plants in the spectrum for Madras is the *Chamaephyte* which is nearly two and a half times that of the normal spectrum (23·5%). The next figure in importance is that of the *Therophyte* which exceeds by only 4 per cent. Therefore the important life-forms for consideration are these two. The last *i.e.* the *Therophytes*, are not so high as in the spectra for the Libyan Desert or Cyrenaica (42 and 50 per cent. respectively) which have according to Raunkiaer, a *Therophyte* climate. Therefore *Therophytes* cannot be said to characterize the Madras climate.

However, if the *Phanerophytes* and *Chamaephytes* are combined, it is found that their percentage exceeds the number in the Normal Spectrum (57 per cent.). As is known⁷, the *Phanerophytes* of Madras are chiefly *Nanophanerophytes* and hence we have a climate characterized by the preponderance of *Nanophanerophytes* and *Chamaephytes*.

* Ph = *Phanerophytes*.

Ch = *Chamaephytes*.

H = *Hemicryptophytes*.

Cr = *Cryptophytes*, *i.e.* *Geophytes*, *Helophytes* and *Hydrophytes*.

Th = *Therophytes*.

In support of this conclusion the example of Aden is quoted for which a similar spectrum was obtained by Raunkiaer⁶ as can be seen from Table 4. So, just as Aden, Madras is an example of which the biological spectrum exhibits conditions on the border regions between the tropical and sub-tropical areas with dry climates. In Madras, as in Aden, the winter temperature is not so low as to be an hindrance to the vital activities of the plants and as such, the evergreen epigeal perennating species xerophytic enough to stand the climate, will be here most favoured.

SUMMARY AND CONCLUSIONS

1. Due to practically no study being done in India on the basis of Raunkiaer's Life-Form system, the present work was undertaken along with those of about five other places in the Deccan.
2. The present bio-statistical study was made possible due to the publication of an exhaustive flora of the Madras City and its Environs by Mayuranathan.
3. The biological spectrum for Madras is then studied in correlation with topography, geology, and especially its climatic features and the following conclusions are drawn:—
 - (a) From the above study it is found that Madras resembles Aden in having a *plant-climate* characterized by the preponderance of Nanophanerophytes and Chamaephytes.
 - (b) That though *climatically* Madras may be said to fall within the tropical region³ due to its mean temperature being 75° F. and its January temperature over 65° F., *plant-climatically* it is a region which exhibits conditions on the border region between the tropical and the sub-tropical, as Aden.

ACKNOWLEDGMENTS

In conclusion we wish to express our deep sense of gratitude to Professor S. P. Agharkar, M.A., Ph.D., F.N.I., for his valuable suggestions and criticisms.

To Rev. Fr. J. Caius, S.J., of St. Xavier's College, we wish to thank for the trouble he has taken over the revision of

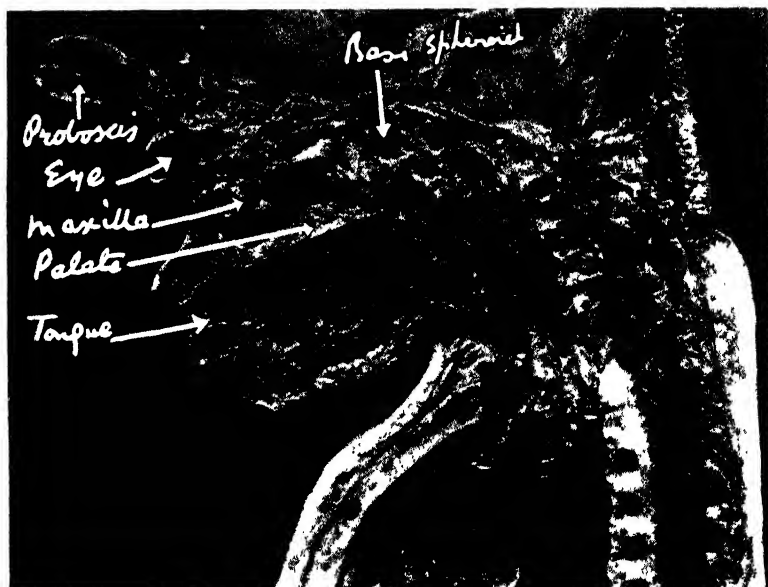
the MSS. and the suggestions he has made from time to time. We also thank the Ex-Director of the Colaba Observatory, Dr. K. R. Ramanathan and Dr. S. R. Savur, the present Director, for supplying us so kindly with the climatic data.

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Front View



Median Sagittal Section

A CASE OF CYCLOPS EYE IN A FULL TERM HUMAN FOETUS

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Front view shows a hollow nasal cavity, within the projecting proboscis, just above the median transversally elongated eye. The Eye shows a single cornea and lens, both transversally elongated. On section, iris showed two apertures for the pupils. Upper eyelid is arched while lower eyelid shows a depression in the middle. Cheeks and lips appear normal.

This baby was cut into two by median sagittal section.

Median sagittal section shows :—Proboscis is hollow. Its outer layer is of skin and inner lining is of mucous membrane. The skin extends for about $\frac{1}{4}$ inch inside the nasal cavity which stops short posteriorly in front of the Glabella.

Above the Proboscis, is frontal bone covered by a thin layer of muscle and subcutaneous tissue. From its lower end extends backwards the orbital plate to form the roof of the orbit. This orbital plate is continued laterally into the lesser wing of the sphenoid while in the middle line there is slight deficiency between it and jugum sphenoid, etc. Under the orbital plate of the frontal bone are ocular muscles surrounding the Eye-ball. The brain matter was decomposed, hence its attachments to the Optic Nerve could not be traced. Just behind the Optic Foramen is seen rounded Basi-Sphenoid joined by a thin plate of cartilage to the Basi-Occiput. Behind this is Foramen Magnum. Below the Eye-ball and orbital contents is seen the orbital surface of the maxillary bone. In the hollows under it were seen germs of milk teeth. These were like hollow capsules. In front of these hollows is the upper lip, while behind these is the rostrum of the Sphenoid bone surrounded by part of the Vomer. Just below this is seen the Palatal bone meeting the palatine process of the

Maxilla just above the tongue. Thus the mouth cavity is distinctly seen getting into the Pharynx and Oesophagus, behind the carotid vessels. The space between Oral Pharynx below, Vertebral Column behind and Basi-Sphenoid, Rostrum, Vomer and Palate anteriorly is filled in by Mesenchyme. Below the Tongue are seen mandible and hyoid bones.

In the Thorax are seen from before backwards, Thymus, Pericardium enclosing chambers of the Heart, Superior and Inferior Venae Cavae. Posteriorly is seen Lung with part of its Hilum showing Bronchus, Pulmonary Veins and Pulmonary Artery.

Diaphragm down below shows clearly its three components, *i.e.* (1) Part derived with pericardium, (2) Septum transversum and (3) Part derived from the Hepatic 'ridge. Inferior Vena Cava is seen getting into the Heart through the diaphragm.

In the Abdomen are seen the following structures :—

Liver lies immediately under the diaphragm. In the Liver is entering patent left Umbilical Vein from below. It is being joined by the Portal Vein. Below this are the cut ends of the Duodenum surrounding the Pancreas. Entering the Posterior end of the Liver is the Inferior Vena Cava. Anterior to the Duodenum and Pancreas are the cut ends of the transverse and descending colon. In front of these are the coils of small intestine. Anteriorly is seen the Navel or Umbilicus showing cut ends of Umbilical Vessels and Patent Urachus.

In the Pelvis is seen anteriorly the Bladder, most of which is an abdominal structure ; behind is the Hind Gut.

DISCUSSION

Proboscis with median Nasal Cavity suggests that Olfactory or Nasal Pit has deepened from the Fronto-Nasal process, but that it stops in front of the frontal bone.

There is no evidence of the Ethmoidal bone, thus the cartilage of the Nasal Capsule has not formed as there is no bony representative of it in front of the Pre-Sphenoid to form Spheno-Ethmoidal plate.

Naso Pharynx has thus not formed. Therefore, in cases like this, breathing is only possible through the mouth.

As regards the Eye, Cornea and Lens were single, thus showing fusion. Pupils were two in one iris, this also proves fusion of two Optic Vesicles.

**List of Theses in Botany, Zoology and Agriculture which have been accepted in lieu of the
Examinations for the Degree of M.Sc., M.Ag. and Ph.D. during the year 1940-41**

Subject	Title of the Thesis	Name of the Candidate	Teacher	Place of Research	Remarks
	FOR THE DEGREE OF M.Sc.				
Botany	Floral Organogeny and Structure and Development of the Micro and Megaspores, their Gametophytes and Embryology in <i>Cissampelos Pareira</i> , <i>Linn.</i>	Mr. R. M. Patel	Prof. S. V. Shevade	Baroda College	
Do.	Life Forms of Plants of the Deccan	Miss D. B. Ferreira	Dr. F. R. Bharucha	R. I. Sc.	Partly published as "The Biological Spectrum of the Madras Flora" in this Issue.
Do.	Ecology of Grasslands at Raika, near Kalyan.	Mr. R. N. Dave	Dr. F. R. Bharucha	R. I. Sc.	
Zoology	The Morphology, Bionomics and Development of a Fish new to Science collected off Bombay Coast. Description and Life History of <i>Horaichthys Setnai</i> Gen and Sp. Nov.	Mr. C. V. Kulkarni	Prof. C. J. George	Wilson College	On the Systematic Position, Structural Modifications, Bionomics and Development of a remarkable new family of Cyprinodont Fishes from the Province of Bombay — Records of the Indian Museum, Calcutta, Vol. XLII, Part II, pp. 379-423.

List of Theses in Botany, Zoology and Agriculture which have been accepted in lieu of the Examinations for the Degrees of M.Sc., M.Ag. and Ph.D. during the year 1940-41—(Contd.)

Subject	Title of the Thesis	Name of the Candidate	Teacher	Place of Research	Remarks
Zoology	Scorpion, its Bionomics and Anatomy.	Mr. V. B. Tembe	Prof. P. R. Awati	R. I. Sc.	
Do.	A Physiological Investigation on the Scorpion Digestive Glands.	Miss J. K. Bardi	Prof. C. J. George	Wilson College	
Agriculture					
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